NOTES ON QUALITATIVE ANALYSIS

CONCISE AND EXPLANATORY

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NOTES ON

QUALITATIVE ANALYSIS

CONCISE AND EXPLANATORY

BY

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PREFACE TO THE NEW EDITION.

IT was the custom at one time to regard the study of Qualitative Analysis as that of a mere art or craft, and the directions which were then provided almost invariably took the form of a list of bare prescriptions or recipes. These were followed by the student in a mechanical and servile manner, and were usually considered by him to be nothing more than arbitrary or empirical rules.

This little book may perhaps claim to be amongst the first in which a serious attempt was made to increase the educational value of the study by enforcing greater attention to its scientific basis. With this object in view the instructions given have been supplemented in all cases by full explanations of the chemical changes involved and of the rationale of the operations performed. It was hoped that in this way the simple experiments which are carried out in the identification of unknown substances might serve, to some extent at any rate, as elementary demonstrations on the general principles of Chemistry. The instructions have been made as concise and simple as possible, and only a minimum of theoretical knowledge is assumed. Minute details of manipulation are, as a rule, not given in full, but are merely suggested or superficially indicated; this course has been followed because it was believed that the custom of providing full practical instructions, which leave nothing for the student to devise or think out for himself,—the 'spoon-feeding' method as it is sometimes styled—is apt to deprive the study of one of its peculiar advantages.

Only the so-called 'common' metals and acids, and the simplest or most typical organic compounds, have been dealt with, the 'rarer' elements being omitted in order to avoid overloading the scheme with material. It is fully conceded that the usual division of the elements into the classes 'common' and 'rare' leaves much to be desired, and that the position

of some of the elements in this classification might with advantage be interchanged; but it appears that a more general agreement on this matter is desirable before one attempts to make the change.

In the present edition the general aim, scope and arrangement of the book remain unchanged; but in view of recent advances and developments in the science, it has been found necessary to make a complete revision of the whole work, and to re-write a considerable portion of it.

The theoretical explanations have been entirely re-cast in order to bring them into harmony with modern views, and the theory of ionic dissociation has been largely incorporated as a working hypothesis. But, at the same time, every effort has been made to avoid even a semblance of dogmatism, and with this object attention is frequently directed to the older explanations; for a similar reason certain compounds, such as basic salts, silicates and metallic hydroxides, are often represented by alternative formulæ.

The practical part has been amplified by the introduction of a considerable number of more recent tests and reactions, and additional alternative methods of separation have been included. Schemes of analysis have been added which deal briefly with the identification of the common gases, the classification of oxides and the preliminary examination of organic substances. The descriptive list of simple organic compounds, with their properties and reactions, has also been enlarged with the object of illustrating at least one example in each of the commoner families.

H. J. H. F.

June 1906.

NOTE. Students who are attempting qualitative analysis for the first time often experience some difficulty in following the complete scheme of analysis owing to the concise form in which the Tables are presented, and also owing to the fact that the scheme is necessarily complicated by the directions for dealing with salts which require special treatment, such as the phosphates and oxalates of the alkaline earths. For such students it has been considered desirable, in the present edition, pp. 46—49, to include two introductory Tables for the identification of single salts of the simpler types. In these Tables, the directions are given in greater detail, chemical symbols are avoided and the number of confirmatory tests is reduced to a bare minimum.

May 1910.

CONTENTS.

PRINCIPAL REACTIONS OF THE MORE COMMON METALS.

The reactions which are given first, and which are printed in the larger type, are those which are employed in the subsequent tables for the systematic separation of the metals or as the principal special tests. The others, printed below in smaller type, are however of considerable importance and should not be neglected.

Most of the changes taking place in aqueous solution which are here represented in equations as double decompositions ($AB + CD = AD + CB$) may, in terms of the ionic dissociation hypothesis, be regarded merely as the reaction between two ions ($A^{\cdot} + B' = AB$), the other two taking practically no part. See page 64.

SILVER.

Solutions of silver salts (*e.g.* $AgNO_3$) give with

Hydrochloric acid (or soluble metallic chlorides) white ppt. of silver chloride,

$$AgNO_3 + HCl = AgCl + HNO_3$$

$$[\text{or } Ag^{\cdot} + Cl' = AgCl].$$

This ppt. is turned violet on exposure to daylight. It is easily soluble in ammonia. Insoluble in HNO_3.

It dissolves easily also in solutions of potassium cyanide or sodium thiosulphate.

Strong solutions of HCl or of soluble chlorides dissolve it appreciably but the resulting solutions are precipitated on dilution.

Potassium chromate, crimson ppt. of silver chromate, soluble in HNO_3,

$$2AgNO_3 + K_2CrO_4 = Ag_2CrO_4 + 2KNO_3.$$

Caustic soda, brown ppt. of silver oxide Ag_2O, easily soluble in HNO_3 and in ammonia.

Ammonia, same ppt. (incomplete), easily soluble in excess forming $[AgNH_3]OH$.

Potassium cyanide, white ppt. of silver cyanide AgCN, easily soluble in excess forming $K[Ag(CN)_2]$. Insoluble in dil. HNO_3.

Sodium phosphate, yellow ppt. of silver phosphate Ag_3PO_4, soluble in ammonia and in acids.

Hydrosulphuric acid, black ppt. of silver sulphide Ag_2S, soluble in hot HNO_3.

LEAD.

Solutions of lead salts (*e.g.* $Pb(NO_3)_2$) give with

Hydrochloric acid, white ppt. of lead chloride, slightly soluble in cold water, more easily in boiling water, insoluble in ammonia,

$$Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3.$$

Hydrosulphuric acid, black ppt. of lead sulphide*,

$$Pb(NO_3)_2 + H_2S = PbS + 2HNO_3.$$

This ppt. dissolves in hot *dilute* HNO_3, forming lead nitrate. *Strong* nitric acid converts it chiefly into white insoluble lead sulphate.

Dilute sulphuric acid, white ppt. of lead sulphate, soluble in strong solution of ammonium acetate or tartrate,

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3.$$

Potassium chromate, yellow ppt. of lead chromate, insoluble in acetic acid, soluble in NaHO,

$$Pb(NO_3)_2 + K_2CrO_4 = PbCrO_4 + 2KNO_3.$$

Potassium iodide, yellow ppt. of lead iodide PbI_2, soluble in boiling water.

Caustic soda, white ppt. of hydrated lead oxide $2PbO . H_2O$, soluble in excess forming $Na_2(PbO_2)$.

Ammonia, white ppt. of basic salt, insoluble in excess.

Solid lead compounds heated on charcoal before the blow-pipe give yellow or orange incrustation, and, in the reducing flame, with Na_2CO_3, metallic beads which are malleable.

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* If much HCl is present the ppt. is often dark red and consists of $PbS . PbCl_2$.

MERCURY.

General Reactions.

Solutions of mercury compounds heated with metallic copper and dilute hydrochloric acid (free nitric acid should be absent) give a bright deposit of metallic mercury on the copper. The product is washed, dried on filter paper and heated in a dry narrow test-tube, when the mercury sublimes forming a grey ring which may be united into globules by rubbing with a glass rod.

The oxy-salts of mercury shew a great tendency to hydrolyse when dissolved in water, giving sparingly soluble basic salts.

Solid mercury compounds heated on charcoal volatilize entirely. Heated in a bulb-tube with dry Na_2CO_3 a ring of metallic mercury is obtained.

Mercurous Salts.

Solutions of mercurous salts (*e.g.* $HgNO_3$) give with

Hydrochloric acid, white ppt. of mercurous chloride (calomel),

$$HgNO_3 + HCl = HgCl^* + HNO_3.$$

This ppt. is blackened by ammonia, owing to the formation of so-called 'dimercurous-ammonium chloride.' This however is perhaps a mixture of metallic mercury with mercuric-ammonium chloride;

$$2HgCl + 2NH_3 = NHgH_2Cl + Hg + NH_4Cl.$$

HgCl is also turned grey when boiled with strong HCl owing to separation of metallic mercury; in this case $HgCl_2$ goes into solution probably with formation of a complex anion, *e.g.*—

$$2HgCl + HCl = H(HgCl_3) + Hg.$$

None of the ordinary solvents will dissolve mercurous chloride unchanged; it dissolves in strong HNO_3 or in aqua regia, but is then converted into mercuric salt.

Caustic soda, black ppt. of mercurous oxide,

$$2HgNO_3 + 2NaOH = Hg_2O + 2NaNO_3 + H_2O.$$

Ammonia, black ppt. probably $NHg''H_2NO_3 . HgO + 2Hg$.

Potassium iodide, greenish yellow ppt. of mercurous iodide HgI, soluble in excess with separation of Hg.

Hydrosulphuric acid, black ppt. of mercuric sulphide mixed with mercury.

Stannous chloride, grey ppt. of metallic mercury.

Potassium chromate, brown ppt. of basic mercurous chromate, changed on boiling to red normal mercurous chromate Hg_2CrO_4.

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* Notwithstanding the large amount of research which has been devoted to the subject, the question as to the molecular state of calomel can scarcely be regarded as finally settled. Probably in the present state of our knowledge it would be more correct to write the formula for solid calomel as Hg_2Cl_2; the single formula HgCl however adequately indicates most of its chemical relationships. Compare Fileti, *J. Pr. Chem.* 1894, *222*; V. Meyer, *Ber.* 1894, *1482* and 1895, *364*; Baker, *Trans. Chem. Soc.* 1900, *646*; Beckmann, *Zeit. Anorg. Chem.* 1907 (55) *175*. See also footnote on page 5.

Mercuric Salts.

Solutions of mercuric salts (*e.g.* $Hg''Cl_2$) give with

Hydrosulphuric acid, black ppt. of mercuric sulphide,

$$HgCl_2 + H_2S = HgS + 2HCl.$$

This ppt. is insoluble in ammonium sulphide and in dilute HNO_3. Strong HNO_3 converts it into a white substance,

$$Hg_3S_2(NO_3)_2 \text{ [or } 2HgS . Hg(NO_3)_2].$$

If the H_2S is passed slowly the ppt. is first white, due to a sulphochloride, this then changes to yellow, brown, and black by further action of H_2S.

Caustic soda, in excess, yellow ppt. of mercuric oxide,

$$HgCl_2 + 2NaOH = HgO + 2NaCl + H_2O.$$

Potassium iodide, red ppt. of mercuric iodide HgI_2, soluble in excess, forming the complex single salt $K_2(HgI_4)$.

Ammonia, white ppt. of mercuric-ammonium chloride $(NHg''H_2)Cl$.

Stannous chloride, first a white ppt. of mercurous chloride, which is afterwards further reduced to metallic mercury, if sufficient $SnCl_2$ is present.

COPPER.

Cupric Salts (usually blue or green).

Solutions of cupric salts (*e.g.* $CuSO_4$) give with

Hydrosulphuric acid, black ppt. of cupric sulphide,

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

This ppt. is nearly insoluble in ammonium sulphide. Soluble in hot dilute HNO_3, forming cupric nitrate $Cu(NO_3)_2$. Insoluble in dilute H_2SO_4. [The precipitation by H_2S is prevented by the presence of potassium cyanide owing to the formation of a complex salt such as $K[Cu(CN)_2$.]

Potassium ferrocyanide, chocolate ppt. of cupric ferrocyanide,

$$2CuSO_4 + K_4(FeC_6N_6) = Cu_2(FeC_6N_6) + 2K_2SO_4.$$

Ammonia, pale greenish-blue ppt. of a basic cupric sulphate [such as $CuSO_4 . 2Cu(OH)_2$], readily soluble in excess of NH_3, forming a dark blue solution. This solution contains a compound having the composition $(CuSO_4 + 4NH_3 + H_2O)$ [or $[Cu(NH_3)_4]SO_4 . H_2O$, the blue colour being due to the cation $Cu(NH_3)_4$].

Caustic soda, pale blue ppt. of cupric hydroxide $Cu(OH)_2$, which turns black on boiling, CuO being formed.

Potassium iodide, dirty white ppt. of cuprous iodide CuI, free iodine being liberated.

Potassium cyanide, brownish-yellow or olive-green ppt. of cupric cyanide $Cu''(CN)_2$, which rapidly loses cyanogen, becoming $Cu'CN$; this dissolves in excess of KCN giving complex salts such as $K[Cu(CN)_2]$ or $K_3[Cu(CN)_4]$ which are colourless.

Many *reducing agents* such as glucose, aldehyde, &c. in presence of caustic alkali, precipitate red cuprous oxide Cu_2O, on heating.

Potassium sulphocyanate in presence of reducing agents, such as SO_2, white precipitate of cuprous sulphocyanate CuCNS, insoluble in dilute acids. [In absence of the reducing agent a black ppt. of cupric sulphocyanate $Cu(CNS)_2$ is obtained if the solutions are sufficiently concentrated.]

Cuprous Salts (usually white, and insoluble in water).

Solutions of cuprous salts (*e.g.* CuCl* dissolved in HCl) give with

Caustic soda, yellow ppt. of cuprous hydroxide Cu(OH); on boiling this changes to red Cu_2O.

Potassium iodide, white ppt. of cuprous iodide *without* separation of iodine,

$$CuCl + KI = CuI + KCl.$$

Water gives a white ppt. of CuCl, this being soluble only in *strong* HCl.

Solid copper compounds heated with Na_2CO_3 on charcoal before the blow-pipe give red globules or spangles of metallic copper.

Borax bead, in oxidising flame, green when hot, blue when cold.

CADMIUM.

Solutions of cadmium salts (*e.g.* $CdCl_2$) give with

Hydrosulphuric acid, bright yellow ppt. of cadmium sulphide,

$$CdCl_2 + H_2S = CdS + 2HCl.$$

This ppt. is insoluble in ammonium sulphide and in potassium cyanide. Soluble in hot dilute HNO_3 forming cadmium nitrate $Cd(NO_3)_2$. Soluble in hot dilute H_2SO_4.

Caustic soda, white ppt. of cadmium hydroxide, insoluble in excess,

$$CdCl_2 + 2NaOH = Cd(OH)_2 + 2NaCl.$$

Potassium cyanide, white ppt. of cadmium cyanide,

$$CdCl_2 + 2KCN = Cd(CN)_2 + 2KCl.$$

This ppt. dissolves in excess forming $K_2[Cd(CN)_4]$ (which however exists in solution partly as ions of the double salt $Cd(CN)_2 . 2KCN$). From this solution H_2S precipitates cadmium sulphide.

Ammonia gives same ppt. as caustic soda (from a sufficiently strong solution) easily soluble in excess.

Solid cadmium compounds heated on charcoal in the reducing flame with Na_2CO_3 give a brown incrustation.

* The vapour density of cuprous chloride even at very high temperatures corresponds to the formula Cu_2Cl_2, but by the vapour pressure method, using bismuth chloride as solvent, the single formula CuCl is indicated. In all other metallic chlorides examined by this method, the molecular weight was found to correspond with the simplest formula. [Rügheimer and Rudolfi, *Annalen*, 1905 (339) *311*. Compare also footnote page 7.]

BISMUTH.

Solutions of bismuth salts (*e.g.* $Bi(NO_3)_3$) give with

Hydrosulphuric acid, blackish-brown ppt. of bismuth sulphide,

$$2Bi(NO_3)_3 + 3H_2S = Bi_2S_3 + 6HNO_3.$$

This ppt. is insoluble in ammonium sulphide. Soluble in hot dilute HNO_3, forming bismuth nitrate $Bi(NO_3)_3$.

Ammonia, white ppt. of bismuth hydroxide (or a basic salt),

$$Bi(NO_3)_3 + 3NH_3 + 3H_2O = Bi(OH)_3 + 3NH_4NO_3.$$

This ppt. dissolves in HCl, forming bismuth chloride $BiCl_3$. Much water added to the solution precipitates white bismuth oxychloride $Bi_2O_3 . BiCl_3$ (simplest formula $BiOCl$),

$$3BiCl_3 + 3H_2O = Bi_2O_3 . BiCl_3 + 6HCl.$$

Bismuth oxychloride dissolves in hydrochloric but not in tartaric acid.

Stannous chloride + caustic soda, black ppt. This appears to be metallic bismuth and not the oxide BiO as was formerly supposed.

Potassium chromate, yellow ppt. of basic bismuth chromate $3Bi_2O_3 . 2CrO_3$, insoluble in KHO, soluble in dilute HNO_3.

Potassium iodide, brown ppt. of bismuth iodide BiI_3, soluble in excess.

Caustic soda, white ppt. of bismuth hydroxide $Bi(OH)_3$.

ARSENIC.

General Reactions.

Compounds of arsenic in solution acidified with HCl (free HNO_3 should be absent*) and introduced into a vessel in which hydrogen is being generated (*e.g.* by the action of Zn + dil. H_2SO_4), give off arseniuretted hydrogen AsH_3†, which burns with a bluish-white flame. If a piece of cold porcelain be held in the flame, a black stain of metallic arsenic is deposited on it. This stain dissolves at once in *sodium hypochlorite*. [Marsh's test.]

[AsH_3 is also slowly evolved if Al and NaOH (strong sol.) are used instead of Zn and H_2SO_4. This is in some cases to be preferred owing to the greater purity of the commercial reagents. (Fleitmann's test.)]

If arseniuretted hydrogen be passed into a solution of silver nitrate, it is decomposed as follows:

$$AsH_3 + 6AgNO_3 + 3H_2O = \underset{\text{black ppt.}}{6Ag} + H_3AsO_3 + 6HNO_3.$$

On carefully neutralizing the clear liquid with ammonia (and adding a drop more $AgNO_3$, if necessary), a yellow ppt. of silver arsenite is obtained (see below).

Solid arsenic compounds heated on charcoal with Na_2CO_3 (or KCy) in the reducing flame give a characteristic (poisonous) odour of garlic.

Heated in a bulb-tube with Na_2CO_3 and charcoal, a black ring of metallic arsenic is obtained. This ring when heated in a dry test-tube gives a crystalline sublimate of arsenic trioxide As_2O_3.

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* Also other oxidising agents. Some other substances also interfere, *e.g.* sulphites, Hg salts, &c. A copper or platinum salt is often added to accelerate the evolution of hydrogen, but this is not to be recommended if mere traces of As are being looked for.

† Also called Arsenic trihydride, or Arsine.

Arsenious Compounds.

Arsenious oxide As_2O_3* is very sparingly soluble in water, giving a weakly acid solution; the formula for the acid which it produces (arsenious acid) is not known. The silver salt corresponds to the ortho acid $As(OH)_3$ but the soluble salts generally correspond to acids of the composition $HAsO_2 (= As_2O_3 . H_2O)$, or $H_4As_2O_5 (= As_2O_3 2H_2O)$. It dissolves easily in alkalies or in HCl. If boiled with strong HCl the arsenic partly vaporises as $AsCl_3$;

$$As_2O_3 + 6HCl \rightleftarrows 2AsCl_3 + 3H_2O.$$

Solutions of arsenious compounds (*e.g.* As_2O_3) give with

Hydrosulphuric acid in presence of dilute HCl, yellow ppt. of arsenious sulphide,

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

[Arsenious acid, in absence of HCl or other electrolytes, gives no ppt. with H_2S, only a yellow colloidal solution; addition of salts, or acids, causes the precipitation of As_2S_3 from this solution.]

This ppt. dissolves in ammonium sulphide, forming a sulpharsenite such as

$$NH_4AsS_2 [= (NH_4)_2S . As_2S_3];$$

and in ammonium carbonate, giving a mixture of arsenite and sulpharsenite. From either of these solutions dilute acids reprecipitate As_2S_3, thus:—

$$2NH_4AsS_2 + 2HCl = As_2S_3 + 2NH_4Cl + H_2S$$

and $$NH_4AsO_2 + 3NH_4AsS_2 + 4HCl = 2As_2S_3 + 4NH_4Cl + 2H_2O.$$

Silver nitrate gives no ppt. with free arsenious acid, but if the solution is just neutralized (*e.g.* with ammonia) it gives a yellow ppt. of silver arsenite,

$$As_2O_3 + 3H_2O + 6AgNO_3 + 6NH_3 = 2Ag_3AsO_3 + 6NH_4NO_3.$$

Ammoniacal copper sulphate, green ppt. of cupric hydrogen arsenite $CuHAsO_3$, soluble in ammonia; this when heated with caustic soda gives red Cu_2O.

Magnesium sulphate, in presence of NH_4Cl and NH_3, no ppt.

Metallic copper, in presence of dilute HCl, steel-grey deposit of copper arsenide which when heated in an open tube gives crystalline sublimate of As_2O_3. [Reinsch's test.]

Oxidising agents, such as nitric acid, sodium hypochlorite, &c. convert arsenio*us* compounds into the arseni*c* form.

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* The vapour density of arsenious oxide was found by Mitscherlich (1830), V. and C. Meyer (1879) and Scott (1887) to correspond with the doubled formula As_4O_6. Biltz however (1895) has shewn that the vapour density diminishes at higher temperatures and at about 1750° corresponds to the single formula As_2O_3. He finds further that the molecular weight in boiling nitrobenzene corresponds to the double formula; in boiling water however the molecules formed contain only one atom of arsenic. There are many other compounds which form polymerised molecules at certain temperatures (or in certain solvents), but it does not follow that the reactions of these substances are more correctly represented by using the complex formulæ. (Compare ferric chloride, stannous chloride, acetic acid, &c.)

Arsenic Compounds.

[Compounds of pentavalent arsenic in solution always contain the arsenic in the acidic part or anion.]

Solutions of arsenic compounds (*e.g.* Na_2HAsO_4 ($= 2Na_2O . H_2O . As_2O_5$)) give with

Hydrosulphuric acid in presence of dilute HCl, slowly, a white ppt. of *sulphur*, the arsenic being reduced to the trivalent condition

$$As_2O_5 + 2H_2S = As_2O_3 + 2H_2O + 2S;$$

by further action of H_2S a yellow ppt. of arsenious sulphide is produced,

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

These changes take place much more readily when the solution is heated.

[Under certain conditions (especially with excess of HCl in the cold) the pentasulphide As_2S_5 is precipitated.]

If the solution is first boiled with SO_2, H_2S will give an immediate ppt. of As_2S_3; it is necessary of course to remove excess of SO_2 by boiling before passing H_2S.

Silver nitrate, brick red ppt. of silver arsenate soluble in ammonia or in acids,

$$Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3.$$

Copper sulphate, greenish blue ppt. of cupric hydrogen arsenate (not reduced on heating with NaOH).
Magnesium sulphate + ammonia, in presence of NH_4Cl, white crystalline ppt. of $Mg(NH_4)AsO_4$.
Ammonium molybdate in presence of HNO_3, yellow ppt. on heating.
Ferric chloride, yellowish white ppt. of $FeAsO_4$. *Calcium chloride*, white ppt. of $CaHAsO_4$.
Many *reducing agents* convert arsenic compounds into the arsenious form:—

e.g. $As_2O_5 + 2SO_2 + 2H_2O = As_2O_3 + 2H_2SO_4$.

ANTIMONY.

General Reactions.

Compounds of antimony in solution acidulated with HCl, and poured on to a piece of *zinc* in contact with *platinum* foil, give a black stain of metallic antimony *on the platinum.*

In *Marsh's apparatus* they behave similarly to compounds of arsenic, but the black stain produced does not dissolve in sodium hypochlorite [nor is SbH_3 evolved if Al and KOH be employed].

Antimoniuretted hydrogen SbH_3* passed into a solution of *silver nitrate* is decomposed as follows:

$$SbH_3 + 3AgNO_3 = \underbrace{SbAg_3}_{\text{black ppt.}\dagger} + 3HNO_3.$$

The Sb may be dissolved out of this ppt. with tartaric acid, and confirmed by $HCl + H_2S$, as below.

Solid antimony compounds heated on charcoal before the blow-pipe with Na_2CO_3, in the reducing flame, give brittle grey metallic globules, and a white incrustation of Sb_2O_3.

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* Also called Antimony trihydride or Stibine.

† Vitali considers that this is a mixture of $Sb(OH)_3$ with metallic silver. (Compare Arsenic.)

Antimonious Compounds.

Solutions of antimonious compounds (*e.g.* $SbCl_3$) give with

Hydrosulphuric acid (in presence of dilute HCl), orange ppt. of antimonious sulphide,

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl.$$

This ppt. dissolves in *ammonium sulphide*, forming an ammonium sulph-antimonite, *e.g.* NH_4SbS_2 or $(NH_4)_3SbS_3$, from which it is reprecipitated by dilute acids; and in strong boiling HCl, forming antimonious chloride $SbCl_3$. It is almost insoluble in ammonium carbonate.

Silver nitrate, in excess, in presence of caustic soda, black ppt. of silver oxide mixed with metallic silver; on treatment with ammonia the latter remains undissolved.

Water gives white ppt. of antimonious oxychloride $Sb_2O_3 . SbCl_3$, soluble in *tartaric acid* and in HCl. HCl gives a similar ppt. from many antimonious compounds (*e.g.* tartar emetic) readily soluble in excess.

Caustic soda, white ppt. of antimonious oxide Sb_2O_3, soluble in excess, forming sodium antimonite $NaSbO_2(=Na_2O . Sb_2O_3)$.

Ammonia gives some ppt. as NaHO, nearly insoluble in excess.

Potassium iodide + HCl give no iodine on heating.

Antimonic Compounds.

Solutions of antimonic compounds (*e.g.* $KSbO_3 = K_2O . Sb_2O_5$) give with

Hydrosulphuric acid, in presence of dilute HCl, orange ppt. consisting chiefly of antimonic sulphide,

$$K_2O . Sb_2O_5 + 2HCl + 5H_2S = Sb_2S_5 + 2KCl + 6H_2O.$$

This ppt. dissolves in *ammonium sulphide*, forming ammonium sulph-antimoniate $(NH_4)_3SbS_4$, from which it is reprecipitated by dilute acids; and in strong boiling HCl, forming antimoni*ous* chloride and free sulphur,

$$Sb_2S_5 + 6HCl = 2SbCl_3 + 3H_2S + S_2.$$

Heated with *potassium iodide* and *hydrochloric acid*, iodine is set free:

$$KSbO_3 + 6HCl + 2KI = SbCl_3 + 3KCl + 3H_2O + I_2.$$

The precipitate produced by *silver nitrate* and *caustic potash* is *soluble* in ammonia.

These last two reactions distinguish antimon*ic* from antimoni*ous* salts.

TIN.

General Reactions.

If a small piece of zinc be added to a solution containing tin acidulated with dilute HCl, a grey deposit of metallic tin is obtained on the zinc. On dissolving this deposit (with the zinc, if necessary), in strong hot HCl, stann*ous* chloride is obtained, which may be confirmed, as below, with mercuric chloride.

Solid tin compounds heated on charcoal with Na_2CO_3 and KCy in the reducing flame give malleable beads of metallic tin. Oxides of tin moistened with cobalt nitrate and heated in the oxidising flame give a bluish-green mass.

Stannous Salts.

Solutions of stannous salts (*e.g.* $SnCl_2$) give with

Hydrosulphuric acid, in presence of dilute HCl, dark brown ppt. of stannous sulphide,

$$SnCl_2 + H_2S = SnS + 2HCl.$$

This ppt. dissolves in *yellow* ammonium sulphide*, forming ammonium sulphostann*ate* $(NH_4)_2SnS_3[=(NH_4)_2S.SnS_2]$ from which dilute HCl precipitates dirty yellow stann*ic* sulphide SnS_2. Stannous sulphide is soluble in strong boiling HCl, forming stannous chloride. Insoluble in *ammonia*.

Mercuric chloride, white ppt. of mercurous chloride, turning to grey metallic mercury if sufficient stannous salt is present, especially on heating,

$$SnCl_2 + 2HgCl_2 = 2HgCl + SnCl_4$$
$$SnCl_2 + 2HgCl = 2Hg + SnCl_4.$$

Auric chloride, purple ppt. (purple of Cassius). This probably consists of a mixture of finely divided gold and SnO_2.

Caustic soda, white ppt. of hydrated stannous oxide $SnO.xH_2O$, soluble in excess, forming sodium stannite $Na_2SnO_2(=Na_2O.SnO)$.

Ammonia, same ppt. as KHO, insoluble in excess.

Stannous salts act as reducing agents, becoming converted into the stannic form; thus *potassium bichromate* or *permanganate* (in acidulated solution) are at once reduced, giving a green chromium salt, and a colourless manganous salt respectively. Silver nitrate gives a black ppt. of metallic silver. Ferric and cupric salts are reduced to the ferrous and cuprous state.

Stannic Salts.

Solutions of stannic salts (*e.g.* $SnCl_4$) give with

Hydrosulphuric acid, in presence of dilute HCl, dirty yellow ppt. of stannic sulphide,

$$SnCl_4 + 2H_2S = SnS_2 + 4HCl.$$

This ppt. dissolves in *ammonium sulphide*, forming ammonium sulphostannate $(NH_4)_2SnS_3$, from which HCl reprecipitates SnS_2. Soluble in strong boiling HCl, forming stannic chloride. Nearly insoluble in *ammonium carbonate*. Soluble in *ammonia*.

Mercuric chloride, no ppt. (Distinction from stann*ous* salts.)

Many *neutral salts* (*e.g.* Na_2SO_4 or NH_4NO_3) give, in dilute solutions, on boiling, white ppt. of metastannic acid and stannic acid†.

Caustic soda, white ppt. of hydrated stannic oxide $SnO_2.xH_2O$, soluble in excess, forming sodium stannate $Na_2SnO_3(=Na_2O.SnO_2)$.

Ammonia, a similar ppt. incompletely soluble in large excess.

Stannic salts may be reduced to the stannous form by *metallic copper* or *tin*, or by reducing to metal by *zinc* and dissolving in strong HCl.

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* The yellow "ammonium sulphide" used in laboratories contains an excess of sulphur, being a mixture of polysulphides of ammonium, ammonium thiosulphate, &c.

† The hydrated stannic oxides $(xSnO_2yH_2O)$ exhibit a remarkable difference in properties according to the method of preparation. The product obtained by action of alkalis on stannic chloride, or of acids on stannates, is soluble in HCl and HNO_3, and is called stannic acid; that obtained by action of strong HNO_3 on tin is insoluble in strong acids, and is called metastannic acid. The latter combines with strong HCl to form a product which is soluble in water and which differs somewhat from stannic chloride in properties; it is called metastannic chloride or β stannyl chloride and appears to be $Sn_5O_5Cl_2(OH)_8$.

IRON.

Ferrous Salts.

Solutions of ferrous salts (*e.g.* $FeSO_4$) give with

Ammonia, dirty green ppt. (white, if pure) of ferrous hydroxide,

$$FeSO_4 + 2NH_3 + 2H_2O = Fe(OH)_2 + (NH_4)_2SO_4.$$

This precipitation is partly prevented by NH_4Cl. The ppt. readily absorbs oxygen from the air, becoming reddish-brown hydrated Fe_2O_3.

Potassium ferricyanide, dark blue ppt. often regarded as ferrous ferricyanide (Turnbull's blue*),

$$3FeSO_4 + 2K_3[FeC_6N_6] = Fe_3''[FeC_6N_6]_2''' + 3K_2SO_4.$$

Potassium ferrocyanide, pale blue ppt. (white, if pure) of ferrous-potassium ferrocyanide,

$$FeSO_4 + K_4[FeC_6N_6] = K_2Fe''[FeC_6N_6] + K_2SO_4.$$

Nitric acid, potassium, permanganate, potassium bichromate and other oxidising agents convert ferr*ous* into ferr*ic* compounds,

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO,$$

$$10FeSO_4 + K_2O . 2MnO . 5O + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O,$$

$$6FeSO_4 + K_2O . Cr_2O_3 . 3O + 7H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O.$$

Potassium sulphocyanate, no colouration with *pure* ferrous salts.

Caustic soda, same result as ammonia.

Ammonium sulphide, black ppt. of ferrous sulphide, soluble in acetic acid.

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* The composition of Prussian blue and Turnbull's blue cannot be considered as finally settled. Later experiments indicate that very probably the two are identical, and that both are ferric ferrocyanide. The composition and properties of these substances depends moreover on the conditions. When a ferrocyanide is added to an excess of ferric salt, or when a ferricyanide is added to an excess of ferrous salt the result is said to be, in either case, ferric ferrocyanide ('Insoluble' Prussian or Turnbull's blue). If however a ferrous salt be added to an excess of ferricyanide, or a ferric salt to an excess of ferrocyanide, the resulting products, which again appear to be identical, have the composition of potassium-ferric ferrocyanide $KFe'''(FeC_6N_6)^{iv}$ (soluble Prussian or Turnbull's blue.)

Ferric Salts.

Solutions of ferric salts (*e.g.* $FeCl_3$) give with

Ammonia, reddish-brown ppt. of hydrated ferric oxide*,

$$FeCl_3 + 3NH_3 + 3H_2O = Fe(OH)_3 + 3NH_4Cl.$$

Potassium ferrocyanide, dark blue ppt. probably ferric ferrocyanide (Prussian blue†),

$$4FeCl_3 + 3K_4[FeC_6N_6] = Fe_4'''[FeC_6N_6]_3^{iv} + 12KCl.$$

Potassium sulphocyanate, blood-red colouration due to ferric sulphocyanate $Fe(CNS)_3$‡. This colour is bleached by mercuric chloride.

Sodium phosphate, yellowish-white ppt. of ferric phosphate,

$$FeCl_3 + Na_2HPO_4 = FePO_4 + 2NaCl + HCl.$$

This ppt. is soluble in HCl but not in acetic acid; hence this precipitation is rendered more complete if sodium acetate is added (compare page 83).

Potassium ferricyanide gives no ppt. only a brown colour.

Ammonium sulphide, black ppt. of ferrous sulphide, free sulphur separating.

Caustic soda, same result as ammonia.

Reducing agents such as H_2S, SO_2, Zn, &c., convert *ferric* into *ferrous* compounds.

Compounds of iron heated in the borax bead give in the oxidising flame an orange yellow while hot, pale yellow when cold. In the reducing flame the bead is bottle-green; this is more easily obtained by starting with a ferrous salt.

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* It is usual to represent the formulæ of precipitated metallic hydroxides, or hydrated oxides, as belonging to the normal type $M^x(OH)_x$ or $M_xO_y . yH_2O$. It is probable that hydroxides of this type are produced in the first instance, but when collected and analysed the ratio of oxide to water in many cases is not in accordance with this type, and may vary with conditions. This fact is indicated by using such formulæ as $xFe_2O_3 . yH_2O$; in writing equations however the normal type is generally given for the sake of simplicity.

† See footnote, page 11.

‡ Or perhaps to the formation of an oxidized condensation product $FeHC_3N_3O_3S_3$. (Tarugi).

CHROMIUM.

Any chromium compound fused with Na_2CO_3 on platinum foil in presence of air (or with addition of a little KNO_3) gives a yellow mass of sodium chromate; *e.g.*

$$Cr_2O_3 + 2Na_2CO_3 + O_3 = 2Na_2CrO_4 + 2CO_2.$$

This may be dissolved in water acidified with acetic acid, and tested for chromate as below with lead acetate.

Before the blow-pipe, chromium compounds give a green borax bead in both flames.

Chromic Salts.

Solutions of chromic salts (*e.g.* Cr_2Cl_6) give with

Ammonia, bluish-green ppt. of chromic hydroxide,

$$CrCl_3 + 3NH_3 + 3H_2O = Cr(OH)_3 + 3NH_4Cl.$$

This ppt. is partly soluble in excess of ammonia, giving a pink solution, but is completely reprecipitated by boiling for some time.

Caustic soda gives same result as ammonia, easily soluble in excess, forming a green solution. Reprecipitated by continued boiling.

Many *oxidising agents*, *e.g.* NaClO, PbO_2, $KMnO_4$, H_2O_2, (in presence of caustic potash), convert chromic salts into chromates.

Ammonium sulphide, bluish-green ppt. of chromic hydroxide $Cr(OH)_3$, with evolution of H_2S.

Sodium phosphate, green ppt. of chromic phosphate $CrPO_4$, soluble in acetic acid, but repptd. on boiling.

Chromates and Bichromates.

Solutions of chromates (*e.g.* K_2CrO_4) give with

Lead acetate, yellow ppt. of lead chromate, insoluble in acetic acid,

$$K_2CrO_4 + (CH_3CO_2)_2Pb = PbCrO_4 + 2CH_3COOK.$$

Silver nitrate, crimson-red ppt. of silver chromate Ag_2CrO_4 soluble in HNO_3.

Barium chloride, yellow ppt. of barium chromate $BaCrO_4$ insoluble in acetic acid.

Mercurous nitrate, brown ppt. of basic mercurous chromate which on boiling turns to the red normal salt Hg_2CrO_4.

Bichromates (*e.g.* $K_2Cr_2O_7$) in most of their reactions closely resemble chromates; acids change chromates to bichromates, and alkalis change bichromates to chromates. These changes appear to be due not to the mere conversion of normal to acid salt, and *vice versa*, but to the fact that the two salts are derived from *different* acids. CrO_4'' ions (yellow) are changed by acids to Cr_2O_7'' (orange)—$2CrO_4'' + 2H^{\cdot} = Cr_2O_7'' + H_2O$—and alkalis produce the contrary effect—$Cr_2O_7'' + 2OH' = 2CrO_4'' + H_2O$.

Solutions of bichromates give with

Hydrosulphuric acid, in presence of HCl, a green solution of chromic chloride and a white ppt. of sulphur,

$$K_2Cr_2O_7 + 8HCl + 3H_2S = 2KCl + 2CrCl_3 + 7H_2O + 3S.$$

Many other reducing agents (*e.g.* stannous chloride, sulphur dioxide, alcohol, ferrous salts) likewise give green solutions of chromic salt,

$$K_2O \cdot Cr_2O_3 \cdot 3O + 3SnCl_2 + 14HCl = 2CrCl_3 + 3SnCl_4 + 2KCl + 7H_2O,$$
$$K_2O \cdot Cr_2O_3 \cdot 3O + 3SO_2 + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + H_2O,$$
$$K_2O \cdot Cr_2O_3 \cdot 3O + 3CH_3CH_2OH + 4H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 3CH_3CHO + 7H_2O,$$
$$K_2O \cdot Cr_2O_3 \cdot 3O + 6FeSO_4 + 7H_2SO_4 = Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O,$$
$$[\text{or as ions, } Cr_2O_7'' + 6Fe^{\cdot\cdot} + 14H^{\cdot} = 2Cr^{\cdot\cdot\cdot} + 6Fe^{\cdot\cdot\cdot} + 7H_2O].$$

Hydrogen dioxide added to a dilute solution, in presence of dilute H_2SO_4 gives an intense blue colour which quickly changes to green with evolution of oxygen; if, however, ether is also added and the mixture is shaken, the blue substance is dissolved out by the ether and is then much more stable. The nature and composition of this so-called 'perchromic acid' is still under investigation; salts have been isolated from the blue solution corresponding to the acid $HCrO_5$, but it is probable that higher oxidation-products may also be formed, such as H_3CrO_7 and H_3CrO_8.

ALUMINIUM.

Solutions of aluminium salts (*e.g.* $Al_2(SO_4)_3$) give with

Ammonia, white gelatinous precipitate of aluminium hydroxide (or sometimes basic salt),

$$Al_2(SO_4)_3 + 6NH_3 + 6H_2O = 2Al(OH)_3 + 3(NH_4)_2SO_4.$$

Aluminium hydroxide when freshly precipitated is somewhat soluble in pure water (as a 'hydrosol'). Hence the precipitation is more complete in presence of salts, such as NH_4Cl, which convert it into the insoluble form.

Caustic soda, same ppt. as ammonia, soluble in excess, forming sodium aluminate $xNa_2O \cdot yAl_2O_3$, and reprecipitated by ammonium chloride,

$$Na_2O \cdot Al_2O_3 + 2NH_4Cl + 2H_2O = Al_2O_3 \cdot 3H_2O + 2NaCl + 2NH_3.$$

Ammonium sulphide, sodium thiosulphate, sodium carbonate, or *barium carbonate* suspended in water, all precipitate aluminium as *hydroxide*, aluminium salts of the acids mentioned being unstable and easily hydrolysed.

Sodium phosphate, white ppt. of aluminium phosphate $AlPO_4$ insoluble in acetic acid, soluble in caustic soda.

Aluminium compounds when heated before the blow-pipe leave a white infusible mass, which when moistened with cobalt nitrate and again heated is coloured bright blue.

ZINC.

Solutions of zinc salts (*e.g.* $ZnSO_4$) give with

Ammonium sulphide, white ppt. of zinc sulphide (often discoloured),

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4.$$

Soluble in dilute HCl, forming zinc chloride $ZnCl_2$. Insoluble in acetic acid. (Distinction from Mn.)

Caustic soda, white ppt. of zinc hydroxide,

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4,$$

easily soluble in excess of *cold* caustic soda, forming sodium zincate $Na_2O . ZnO$, from which H_2S precipitates white zinc sulphide ZnS. On boiling the solution of sodium zincate, $Zn(OH)_2$ is reprecipitated, especially if dilute.

Ammonia, same ppt. as caustic soda, soluble in excess, and in ammonium chloride, forming ($Zn\ xNH_3$) ions.

Hydrosulphuric acid, white ppt. of ZnS in *alkaline* solution, or one containing only *acetic* acid. No ppt. in presence of sufficient free HCl, H_2SO_4, or HNO_3. [See page 68.]

Potassium ferrocyanide, white ppt. of zinc ferrocyanide, insoluble in dilute HCl.

Potassium ferricyanide, orange ppt. soluble in HCl.

Solid zinc compounds heated on charcoal before the blow-pipe with Na_2CO_3 give a residue which is yellow while hot, white when cold. This residue, when moistened with cobalt nitrate and again heated, gives a bright green mass.

MANGANESE.

General Reactions.

Any compound of manganese when fused in platinum foil with Na_2CO_3 in presence of air (or with addition of a little KNO_3) give a blue-green mass of sodium manganate, *e.g.*

$$MnSO_4 + 2Na_2CO_3 + O_2 = Na_2MnO_4 + Na_2SO_4 + 2CO_2.$$

All compounds of manganese after boiling with strong HCl, give the reactions of mangan*ous* salts.

Traces of manganese compounds (in absence much of Cl or Br) when boiled with nitric acid and peroxide of lead, give a pink colour, due to permanganic acid $HMnO_4$.

In the borax bead manganese compounds give a violet colour in the oxidising flame, colourless in reducing flame.

Manganous Salts.

Solutions of manganous salts (*e.g.* $MnCl_2$) give with

Ammonium sulphide, buff or pinkish ppt. of manganous sulphide,

$$MnCl_2 + (NH_4)_2S = MnS + 2NH_4Cl.$$

This ppt. dissolves in dilute HCl, forming manganous chloride $MnCl_2$. Soluble also in acetic acid. Not precipitated in presence of large excess of ammonia.

Caustic soda, white ppt. of manganous hydroxide, insoluble in excess,

$$MnCl_2 + 2NaOH = Mn(OH)_2 + 2NaCl.$$

This ppt. rapidly absorbs oxygen from the air, forming brown hydrated sesquioxide $Mn_2O_3 . H_2O$*.

Ammonia, same ppt. as caustic soda. No ppt., however, in presence of ammonium chloride (compare Magnesium); this solution readily absorbs oxygen from the air, brown $Mn_2O_3 . H_2O$ being precipitated.

Sodium hypochlorite, dark brown ppt. of hydrated manganese dioxide $MnO_2 . H_2O$*.

Hydrosulphuric acid gives no ppt. in presence of a free acid, even acetic. In alkaline solution MnS is precipitated.

Manganic Salts.

These are mostly very unstable, and easily hydrolyse when dissolved in water. They form red or violet solutions in acids.

Heated with hydrochloric acid they evolve chlorine, *e.g.*

$$Mn_2(SO_4)_3 + 2HCl = 2MnSO_4 + H_2SO_4 + Cl_2.$$

Caustic soda gives a dark brown ppt. of hydrated manganese sesquioxide,

$$Mn_2(SO_4)_3 + 6NaOH = Mn_2O_3 . 3H_2O† + 3Na_2SO_4.$$

---

* The composition of these brown hydrated oxides varies considerably with the conditions, the general formulæ being $xMnO . yMnO_2 . zH_2O$.

† See footnote, page 12.

Manganates and Permanganates.

Solutions of manganates (*e.g.* $K_2MnO_4 = K_2O . MnO_3$) are green; those of permanganates (*e.g.* $KMnO_4$ or $K_2Mn_2O_8 = K_2O . Mn_2O_7$)* rose or purple.

Manganates in solution are very unstable, except in presence of free alkali. In neutral solution they slowly decompose as follows:

$$\underbrace{3(K_2O . MnO_3)}_{\text{green solution}} + 3H_2O = \underbrace{K_2O . Mn_2O_7}_{\text{pink solution}} + \underbrace{MnO_2 . H_2O}_{\text{brown ppt.}} + 4KHO.$$

In presence of dilute acid a similar change takes place immediately, but in this case a manganous salt is formed instead of the brown ppt.

Chlorine also converts manganates into permanganates,

$$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl,$$

$$[\text{or, as ions, } 2MnO_4'' + Cl_2 = 2MnO_4' + 2Cl'].$$

Permanganates boiled with alkalis become manganates, oxygen being evolved,

$$4KMnO_4 + 4KOH = 4K_2MnO_4 + 2H_2O + O_2.$$

Permanganates (or manganates) when heated with strong *sulphuric acid* evolve oxygen,

$$2(K_2O . 2MnO . 5O) + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2;$$

and with strong *hydrochloric acid* evolve chlorine,

$$K_2O . 2MnO . 5O + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

In presence of free acid, they convert—

Ferrous salts into ferric salts,

$$10Fe''SO_4 + 5H_2SO_4 + 5O = 5Fe'''_2(SO_4)_3 + 5H_2O.$$

Stannous salts into stannic salts,

$$5SnCl_2 + 5Cl_2 = 5SnCl_4.$$

Oxalic acid into carbon dioxide and water,

$$5\begin{cases}COOH\\COOH\end{cases} + 5O = 10CO_2 + 5H_2O.$$

Nitrous acid into nitric acid,

$$5HNO_2 + 5O = 5HNO_3.$$

Sulphurous acid into sulphuric acid,

$$5H_2SO_3 + 5O = 5H_2SO_4.$$

The above equations merely indicate the numerical relationships; there is of course no need to assume the initial formation of oxygen or chlorine when permanganates act in this way as oxidising agents. Thus the action on ferrous salts might be represented as

$$MnO_4' + 5Fe^{\cdot\cdot} + 8H^{\cdot} = Mn^{\cdot\cdot} + 5Fe^{\cdot\cdot\cdot} + 4H_2O.$$

---

* There is now but little doubt that potassium permanganate should be represented by the single formula $KMnO_4$. The *composition* of the pink permanganate ion $(MnO_4)'$ and the green manganate ion $(MnO_4)''$ is therefore the same, although the valencies are different.

NICKEL.

Solutions of nickel salts (*e.g.* $NiSO_4$) give with

Ammonium sulphide, black ppt.,

$$NiSO_4 + (NH_4)_2S = NiS + (NH_4)_2SO_4.$$

This ppt. is nearly insoluble in dilute HCl. Soluble in aqua regia, forming nickel chloride $NiCl_2$. Somewhat soluble in excess of ammonium sulphide (especially yellow), forming a dark-coloured solution. [It may be reprecipitated from this solution by adding ammonium acetate and boiling, or by acidifying with acetic acid.]

Caustic soda, pale green ppt. of nickelous hydroxide, insoluble in excess, soluble in ammonium salts,

$$NiSO_4 + 2NaOH = Ni(OH)_2 + Na_2SO_4.$$

Potassium cyanide (pure), greenish-yellow ppt. of nickelous cyanide,

$$NiSO_4 + 2KCN = Ni(CN)_2 + K_2SO_4.$$

This ppt. redissolves easily in excess of potassium cyanide, forming a complex single cyanide $K_2[Ni(CN)_4]$, which is not altered by boiling with excess of KCN in presence of air; it is not very stable, however, the solution behaving partly as a double salt $Ni(CN)_2 . 2KCN$.

This solution gives a pale green ppt. with mercuric oxycyanide*, and a black ppt. with sodium hypochlorite on gently warming, thus

$$Ni(CN)_2 + HgO . Hg(CN)_2 + H_2O = \underbrace{Ni(OH)_2}_{\text{greenish ppt.}} + 2Hg(CN)_2$$

$$2Ni(CN)_2 + NaClO + 5H_2O = \underbrace{2Ni(OH)_3}_{\text{black ppt.}\dagger} + NaCl + 4HCN.$$

Dimethyl glyoxim, bright red ppt. or colouration. See p. 89.

Potassium nitrite, in presence of acetic acid no ppt.

Ammonia, greenish ppt. of nickelous hydroxide, soluble in excess, forming a blue solution. Soluble in ammonium salts.

Hydrosulphuric acid, no ppt. in presence of free HCl.

Potassium ferricyanide, yellowish-brown ppt. of nickel ferricyanide, soluble in *ammonia*.

Ammonium sulphocyanate gives no blue colour. [See Cobalt.]

Nickel compounds give, in the borax bead, a brownish-violet colour in the oxidising flame, often grey in the reducing flame.

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* Prepared by boiling mercuric oxide (freshly pptd.) with solution of mercuric cyanide and filtering.

† The composition varies with conditions. It is usually a mixture of $Ni(OH)_2$, NiO_2 and Ni_2O_3.

COBALT.

Solutions of cobaltous salts (*e.g.* $Co(NO_3)_2$) give with

Ammonium-sulphide, black ppt. of cobalt sulphide,

$$Co(NO_3)_2 + (NH_4)_2S = CoS + 2NH_4NO_3.$$

This ppt. is almost insoluble in dilute HCl, but dissolves in aqua regia, forming cobaltous chloride $CoCl_2$.

Caustic soda, blue ppt. of a basic salt $[Co(NO_3)_2 xCo(OH)_2]$, which, when heated with excess of caustic soda, changes to pink cobaltous hydroxide $Co(OH)_2$. This on exposure to air turns green, grey, or brown, owing to formation of cobaltic hydroxide $Co(OH)_3$.

Potassium cyanide, reddish-brown ppt. of cobaltous cyanide,

$$Co(NO_3)_2 + 2KCN = Co(CN)_2 + 2KNO_3.$$

This ppt. dissolves easily in excess of KCN, forming a complex single cyanide (brown solution),

$$Co(CN)_2 + 4KCN = K_4[Co(CN)_6]. \quad \text{Potassium cobalto-cyanide.}$$

This salt is not very stable, and behaves partly as $4KCN . Co(CN)_2$, since $Co(CN)_2$ is pptd. on addition of acids. But when heated in presence of air the solution becomes colourless, oxygen is absorbed and potassium cobalti-cyanide is formed; this is no longer precipitated by acids, and shews no reaction of cobalt ions,

$$2K_4[Co(CN)_6]^{iv} + H_2O + O = 2K_3[Co(CN)_6]''' + 2KOH.$$

This solution gives no precipitate when warmed with NaClO or with mercuric oxycyanide.

Potassium nitrite (concentrated solution) in presence of acetic acid, yellow crystalline ppt. of potassium cobalti-nitrite. (Slowly in dilute solutions),

$$Co(NO_3)_2 + 5KNO_2 + 2HNO_2 = K_3[Co(NO_2)_6] + 2KNO_3 + H_2O + NO.$$

Ammonium sulphocyanate (concentrated solution), blue colour due to $(NH_4)_2[Co(CNS)_4]$. The latter is unstable, and on dilution gives only the pink colour due to cobaltous ions; but on shaking with ether (or better, a mixture of amyl alcohol and ether), the blue compound is again formed in the ethereal layer.

Ammonia in small quantity gives the same result as caustic soda soluble in excess; no ppt. in presence of NH_4Cl. The ammoniacal solution slowly absorbs oxygen from the air, giving complex cobalti-ammonium compounds.

Potassium ferricyanide, reddish-brown ppt. of cobaltous ferricyanide, insoluble in ammonia.

Cobalt compounds give, in the borax bead, a blue colour in both flames.

BARIUM.

Solutions of barium salts (*e.g.* $BaCl_2$) give with

*Ammonium carbonate**, white ppt. of barium carbonate,

$$BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl,$$

soluble in *dilute* HCl or HNO_3.

Calcium sulphate, immediate white ppt. of barium sulphate,

$$BaCl_2 + CaSO_4 = BaSO_4 + CaCl_2.$$

Hydrofluosilicic acid, colourless crystalline ppt. of barium silicofluoride,

$$BaCl_2 + H_2SiF_6 = BaSiF_6 + 2HCl,$$

somewhat soluble in dilute acids, unless alcohol be added.

Potassium chromate, yellow ppt. of barium chromate, even in dilute solutions,

$$BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl,$$

nearly insoluble in *acetic* acid. Soluble in HCl.

Barium salts are precipitated from their solutions by strong HCl or HNO_3. Barium chloride is insoluble in alcohol.

Dilute sulphuric acid, or any soluble sulphate, even in very dilute solutions, white ppt. of barium sulphate $BaSO_4$, insoluble in dilute acids.

Sodium phosphate, white ppt. of barium phosphate, soluble in dil. HCl, HNO_3, and acetic acid.

Ammonium oxalate, white ppt. of barium oxalate $Ba(CO_2)_2$, soluble in HCl, sparingly soluble in cold acetic acid.

Barium compounds moistened with HCl, and held in the edge of a Bunsen flame on platinum wire, give an apple-green colour.

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* Commercial ammonium carbonate consists principally of the so-called sesquicarbonate

$$2(NH_4)_2O \cdot 3CO_2 \cdot H_2O = (NH_4)_2CO_3 + 2NH_4HCO_3,$$

but it contains also ammonium carbamate $CO(NH_2) \cdot ONH_4$, which is formed from the normal carbonate by loss of water. Since the bicarbonates and the carbamates of Ca, Sr and Ba are soluble, their precipitation by the laboratory reagent is incomplete unless the mixture is heated.

CALCIUM.

Solutions of calcium salts (*e.g.* $CaCl_2$) give with

Ammonium carbonate, white ppt. of calcium carbonate,

$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl.$$

Calcium sulphate, no ppt.

Hydrofluosilicic acid, no ppt.

Potassium chromate, no ppt.

Ammonium oxalate, white ppt. of calcium oxalate, even in very dilute solutions,

$$CaCl_2 + \begin{cases} CO_2NH_4 \\ CO_2NH_4 \end{cases} = \begin{cases} CO_2 \\ CO_2 \end{cases} Ca + 2NH_4Cl.$$

This ppt. is insoluble in *acetic acid;* soluble in dilute HCl or HNO_3.

Calcium chloride and calcium nitrate are both soluble in absolute alcohol.

Sulphuric acid or *soluble sulphates*, white ppt. of calcium sulphate in strong solution only. Readily soluble in strong (ammoniacal) solution of *ammonium sulphate*, forming $(NH_4)_2[Ca(SO_4)_2]$.

Sodium phosphate, white ppt. of calcium phosphate, soluble in HCl, HNO_3, and acetic acid.

Calcium compounds, examined by the flame test, give an orange-red colour.

STRONTIUM.

Solutions of strontium salts (*e.g.* $Sr(NO_3)_2$) give with

Ammonium carbonate, white ppt. of strontium carbonate,

$$Sr(NO_3)_2 + (NH_4)_2CO_3 = SrCO_3 + 2NH_4NO_3.$$

Calcium sulphate, white ppt. of strontium sulphate *after a time*, or on heating,

$$Sr(NO_3)_2 + CaSO_4 = SrSO_4 + Ca(NO_3)_2.$$

Hydrofluosilicic acid, no ppt.

Potassium chromate, no ppt. in dilute solutions.

Strontium chloride is soluble in absolute alcohol; strontium nitrate insoluble.

Dilute sulphuric acid or *soluble sulphates*, white ppt. of strontium sulphate insoluble in strong solution of *ammonium sulphate* (ammoniacal).

Ammonium oxalate, white ppt. of strontium oxalate $Sr(CO_2)_2$, sparingly soluble in acetic acid, soluble in HCl.

Sodium phosphate, white ppt. of strontium phosphate, soluble in HCl, HNO_3, and acetic acid.

Strontium compounds, examined by the flame test, give a characteristic crimson colour.

MAGNESIUM.

Solutions of magnesium salts (*e.g.* $MgSO_4$) give with

Sodium phosphate, in presence of ammonia (and ammonium chloride*), white crystalline ppt. of magnesium ammonium phosphate,

$$MgSO_4 + Na_2HPO_4 + NH_3 = MgNH_4PO_4 + Na_2SO_4.$$

From very dilute solutions this ppt. appears only after some time; stirring accelerates its formation.

Ammonia, white ppt. of magnesium hydroxide (in part),

$$MgSO_4 + 2NH_3 + 2H_2O = Mg(OH)_2 + (NH_4)_2SO_4,$$

but no ppt. in presence of sufficient ammonium chloride. The reason for this is explained on page 69.

Ammonium carbonate, white ppt. of basic magnesium carbonate, but no ppt. in presence of sufficient ammonium chloride.

Barium hydroxide, in absence of ammonium salts, white ppt. of magnesium hydroxide $Mg(OH)_2$.
Caustic soda, same ppt.

Some magnesium compounds (*e.g.* oxide, sulphate, carbonate) heated on charcoal, moistened with cobalt nitrate, and again heated, give a pale rose colour.

AMMONIUM.

Ammonium compounds (*e.g.* NH_4Cl), when boiled with caustic potash. evolve ammonia,

$$NH_4Cl + KOH = KCl + H_2O + NH_3.$$

The ammonia may be recognized by its odour and action on red litmus.

Solutions of ammonium salts give with

Hydrochloro-platinic acid † (in presence of HCl if necessary), yellow ppt. of ammonium platini-chloride,

$$2NH_4Cl + H_2PtCl_6 = (NH_4)_2PtCl_6 + 2HCl.$$

This precipitation is more complete in presence of alcohol. When this ppt. is heated to redness it leaves only metallic platinum.

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* To prevent the precipitation of $Mg(OH)_2$ by ammonia alone.

† So-called platinic chloride solution. See page 93.

Ammonium (*continued*).

Nessler's solution (potassium mercuric iodide with excess of caustic potash) gives, even in very dilute solutions, a brown or yellow coloration (or precipitate in stronger solutions) due to dimercuric-ammonium iodide,

$$NH_4Cl + 2K_2(HgI_4) + 4KOH = NHg_2''I \cdot H_2O + 7KI + KCl + 3H_2O.$$

Tartaric acid, white crystalline ppt. on shaking (in strong solutions) of ammonium hydrogen tartrate

$$\begin{array}{l} COONH_4 \\ \dot{C}HOH \\ \dot{C}HOH \\ \dot{C}OOH \end{array}$$

Ammonium compounds heated before the blow-pipe volatilize entirely or in part.

POTASSIUM.

Solutions of potassium salts (*e.g.* KCl) if not too dilute, give with

*Hydrochloro-platinic acid**, yellow crystalline ppt. of potassium platinichloride, especially on stirring. More complete in presence of alcohol,

$$2KCl + H_2PtCl_6 = K_2PtCl_6 + 2HCl.$$

This ppt. when heated to redness leaves metallic platinum mixed with potassium chloride.

Tartaric acid, white crystalline ppt. of potassium hydrogen tartrate, especially on shaking or stirring. More complete in presence of sodium acetate and alcohol. Easily soluble in HCl, very sparingly soluble in acetic acid, soluble in alkalis.

$$KCl + \begin{array}{l} COOH \\ \dot{C}HOH \\ \dot{C}HOH \\ \dot{C}OOH \end{array} = \begin{array}{l} COOK \\ \dot{C}HOH \\ \dot{C}HOH \\ \dot{C}OOH \end{array} + HCl.$$

Perchloric acid, white crystalline ppt. of potassium perchlorate $KClO_4$.

Sodium cobalti-nitrite, in acetic acid solution, yellow crystalline ppt. of potassium sodium cobalti-nitrite $K_2Na[Co(NO_2)_6]$.

Hydrofluosilicic acid in excess, white gelatinous ppt. of potassium silicofluoride K_2SiF_6.

Potassium salts, examined by the flame reaction, give a violet colour, visible through blue glass.

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* So-called platinic chloride solution. See page 93.

SODIUM.

Solutions of sodium compounds (*e.g.* NaCl) give no characteristic reaction with any of the common reagents, nearly all sodium salts being soluble in water.

Dihydroxytartaric acid, when neutralized with ammonia or potassium carbonate, white crystalline ppt. of sodium dihydroxytartrate $Na_2C_4H_4O_8 . 3H_2O$, even in dilute solutions, on stirring. Potassium, ammonium, or magnesium salts do not interfere except in strong solutions.

Acid potassium pyroantimonate, white ppt. of acid sodium pyroantimonate $Na_2H_2Sb_2O_7$. The reagent must be freshly prepared, and free acids absent.

Sodium compounds give a strong yellow colour to the flame; this is invisible when viewed through cobalt-blue glass.

PRINCIPAL REACTIONS OF THE MORE COMMON ACID RADICLES.

SULPHATES.

Heated with strong H_2SO_4, no result.

Solutions of sulphates (*e.g.* K_2SO_4) give with

Barium chloride, white ppt. of barium sulphate, *insoluble* in HCl or HNO_3,

$$K_2SO_4 + BaCl_2 = BaSO_4 + 2KCl.$$

Strontium chloride (or nitrate), white ppt. of strontium sulphate, $SrSO_4$ (slowly in dilute solutions).

Calcium chloride, white ppt. of calcium sulphate $CaSO_4$, in strong solution only; soluble in much water.

Lead acetate, white ppt. of lead sulphate $PbSO_4$, soluble in *ammonium acetate* or ammonium tartrate.

Dry sulphates (like all sulphur compounds), when heated with sodium carbonate and charcoal in the reducing flame, give sodium sulphide, which when placed on a silver coin and moistened with water, gives a black stain of silver sulphide Ag_2S.

PERSULPHATES.

(*E.g.* $K_2S_2O_8$.) Heated in the dry state they give off oxygen,

$$2K_2S_2O_8 = 2K_2S_2O_7 + O_2.$$

Solutions of persulphates decompose slowly in the cold, quickly on heating, giving off oxygen (partly as ozone) and forming sulphates,

$$2K_2S_2O_8 + 2H_2O = 4KHSO_4 + O_2.$$

They act as powerful oxidising agents to KI or $FeSO_4$ and precipitate higher oxides from salts of Mn, Pb, Ni, and Co. $AgNO_3$ gives a black ppt. of $AgHSO_5$ or Ag_2O_2.

Barium chloride gives no ppt. (unless decomposition has taken place as above).

Potassium permanganate is not decolorised, and *chromic acid* gives no blue colour (distinctions from H_2O_2).

Dissolved in concentrated H_2SO_4 at 0° they give Caro's acid, H_2SO_5. See Supplement, page 174.

SULPHITES.

(*E.g.* Na_2SO_3.) Heated with HCl, sulphur dioxide is evolved,

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2.$$

The evolved gas may be recognized by its odour, and action on $K_2Cr_2O_7$,

$$\underset{\text{(orange)}}{K_2Cr_2O_7} + H_2SO_4 + 3SO_2 = K_2SO_4 + \underset{\text{(green)}}{Cr_2(SO_4)_3} + H_2O.$$

Treated with HCl and *metallic zinc*, hydrosulphuric acid is evolved (detected by lead acetate, &c.),

$$Zn + 2HCl = ZnCl_2 + H_2$$

and $$SO_2 + 3H_2 = 2H_2O + H_2S.$$

Solutions of sulphites give with

Barium chloride, white ppt. of barium sulphite,

$$Na_2SO_3 + BaCl_2 = BaSO_3 + 2NaCl,$$

easily soluble in dilute HCl; from this solution oxidising agents (*e.g.* chlorine water), precipitate white barium sulphate, insoluble in HCl,

$$BaSO_3 + H_2O + Cl_2 = BaSO_4 + 2HCl.$$

Silver nitrate, white ppt. of silver sulphite Ag_2SO_3, soluble in dilute HNO_3; soluble also in excess of sodium sulphite forming the complex salt $Na(AgSO_3)$. When silver sulphite is heated with water it darkens, owing to separation of metallic silver,

$$2Ag_2SO_3 = 2Ag + Ag_2SO_4 + SO_2.$$

Free iodine is decolorized, thus:

$$Na_2SO_3 + H_2O + I_2 = Na_2SO_4 + 2HI.$$

THIOSULPHATES.

Formerly called Hyposulphites.

(*E.g.* $Na_2S_2O_3$.) Treated with HCl, sulphur dioxide is evolved, and yellow sulphur separates, especially on heating,

$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + SO_2 + S.$$

Treated with metallic zinc in excess and HCl, H_2S is evolved as with sulphites, especially on heating.

Thiosulphates (*continued*).

Solutions of thiosulphates give with

Lead acetate, white ppt. of lead thiosulphate,

$$Na_2S_2O_3 + (CH_3CO_2)_2Pb = PbS_2O_3 + 2CH_3COONa.$$

This ppt. on heating blackens, owing to formation of lead sulphide,

$$PbS_2O_3 + H_2O = PbS + H_2SO_4.$$

Silver and *mercurous* salts behave similarly. Silver thiosulphate dissolves in excess of sodium thiosulphate, giving the complex salts,

$$Na(AgS_2O_3) \text{ and } Na_4[Ag_2(S_2O_3)_3].$$

Free iodine is at once decolorized,

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI,$$

$$(\text{as ions, } 2S_2O_3'' + I_2 = S_4O_6'' + 2I').$$

Ferric chloride gives first a transient violet coloration, and is afterwards reduced to ferrous chloride,

$$2Na_2S_2O_3 + 2FeCl_3 = 2NaCl + 2FeCl_2 + Na_2S_4O_6.$$

SULPHIDES.

Heated alone in a current of air (*e.g.* in an open tube) sulphur dioxide is evolved.

Treated with HCl, many sulphides evolve hydrosulphuric acid. [Some require boiling with strong acid; others (*e.g.* FeS_2) are not decomposed unless zinc be added.]

$$FeS + 2HCl = FeCl_2 + H_2S.$$

The evolved gas is recognized by its odour, action on lead acetate, &c.

Soluble sulphides* (*e.g.* $(NH_4)_2S$), give with

Lead acetate, black ppt. of lead sulphide,

$$(NH_4)_2S + (CH_3CO_2)_2Pb = PbS + 2CH_3COO(NH_4).$$

Silver nitrate, black ppt. of silver sulphide Ag_2S insoluble in cold nitric acid or in ammonia.

Sodium nitroprusside, $Na_2[Fe(CN)_5NO]$, gives a fine purple coloration, probably due to a double salt of the sulphide and nitroprusside. Free H_2S does not give the reaction.

Metallic silver is stained black owing to formation of silver sulphide Ag_2S.

* In dilute solution these exist principally as hydrosulphides,

$$Na_2S + H_2O = NaOH + NaSH \ (\textit{i.e.} \text{ as } 2Na^{\cdot}, OH' \text{ and } SH').$$

SILICOFLUORIDES.

(*E.g.* K_2SiF_6.) Heated in a platinum vessel with strong H_2SO_4 evolve silicon tetrafluoride and hydrofluoric acid gases,

$$K_2SiF_6 + H_2SO_4 = K_2SO_4 + SiF_4 + 2HF.$$

SiF_4 deposits white hydrated silica on a wet rod, and HF will etch glass. [See Fluorides.]

Solutions of silicofluorides, or hydrofluosilicic acid, give with

Barium chloride, colourless crystalline ppt. of barium silicofluoride,

$$H_2SiF_6 + BaCl_2 = BaSiF_6 + 2HCl.$$

This ppt. is nearly insoluble in dilute HCl.

Strontium chloride, no ppt.

Potassium chloride, gelatinous ppt. of potassium silicofluoride,

$$H_2SiF_6 + 2KCl = K_2SiF_6 + 2HCl.$$

FLUORIDES.

(*E.g.* CaF_2.) Heated in a platinum vessel with concentrated H_2SO_4 evolve hydrofluoric acid,

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The evolved gas will corrode glass, owing to its action on silica,

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

Heated with concentrated H_2SO_4 in presence of *silica* or silicates, *e.g.* in a test-tube, silicon tetrafluoride is evolved:

$$2CaF_2 + 2H_2SO_4 + SiO_2 = 2CaSO_4 + 2H_2O + SiF_4.$$

A wet rod held in this gas becomes coated with hydrated silica,

$$3SiF_4 + 4H_2O = \underset{\text{white deposit}}{SiO_2 . 2H_2O} + 2H_2SiF_6.$$

Solutions of fluorides (*e.g.* NaF) give with

Calcium chloride, white gelatinous ppt. of calcium fluoride,

$$2NaF + CaCl_2 = CaF_2 + 2NaCl.$$

Sparingly soluble in HCl; nearly insoluble in *acetic* acid, but soluble in ammonium chloride.

Barium chloride, white ppt. of barium fluoride BaF_2, soluble in ammonium chloride.

OXALATES.

$\left(E.g. \begin{cases}COOK \\ COOK\end{cases}.\right)$ Heated with strong H_2SO_4, carbon monoxide and carbon dioxide are evolved,

$$\begin{cases}COOK \\ COOK\end{cases} + H_2SO_4 = K_2SO_4 + CO + CO_2 + H_2O.$$

The CO will burn with a blue flame, and the CO_2 may be detected by lime water. [See Carbonates.]

Treated with H_2SO_4 and manganese dioxide, carbon dioxide alone is evolved,

$$\begin{cases}COOK \\ COOK\end{cases} + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + 2CO_2.$$

Heated alone, oxalates of K, Na, Ba, Sr, Ca, give carbonates and CO; others generally give the metal, or oxide, and CO_2.

Solutions of oxalates give with

Calcium chloride, white ppt. of calcium oxalate,

$$\begin{cases}COOK \\ COOK\end{cases} + CaCl_2 = \begin{cases}COO \\ COO\end{cases}Ca + 2KCl,$$

soluble in HCl, but insoluble in *acetic* acid. This ppt. is produced even in very dilute solutions.

Barium chloride and *strontium chloride*, white ppts. of barium oxalate $(CO_2)_2Ba$ and strontium oxalate $(CO_2)_2Sr$ respectively.

Silver nitrate, white ppt. of silver oxalate $\begin{cases}COOAg \\ COOAg\end{cases}$, soluble in dilute HNO_3.

For reaction with *permanganates* see page 17.

PHOSPHATES.

Orthophosphates.

Heated with strong H_2SO_4, no result.

Solutions of orthophosphates (*e.g.* Na_2HPO_4)* give with

Calcium chloride, white ppt. of calcium hydrogen phosphate,

$$Na_2HPO_4 + CaCl_2 = CaHPO_4 + 2NaCl,$$

soluble in HCl, HNO_3, and acetic acid.

[If ammonia is added, $Ca_3(PO_4)_2$ is precipitated instead of $CaHPO_4$.]

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* Orthophosphoric acid in solution may behave either as a mono-, di- or tri-basic acid according to concentration and other circumstances, *i.e.* the ions may be PO_4''', HPO_4'' or H_2PO_4'. Thus Na_3PO_4 dissolved in water $= 3Na^{\cdot} + PO_4'''$, but $PO_4''' + H_2O = HPO_4'' + OH'$, and, to some extent, $HPO_4'' + H_2O = H_2PO_4' + OH'$.

Orthophosphates (*continued*).

Ferric chloride, yellowish-white ppt. of ferric phosphate,

$$2Na_2HPO_4 + Fe_2Cl_6 = 2Fe(PO_4) + 4NaCl + 2HCl,$$

soluble in HCl or HNO_3, insoluble in *acetic* acid. [This precipitation, in case of acid phosphates as above, is therefore incomplete unless the HCl be neutralized or replaced by acetic acid. For more complete explanation see page 83.]

Magnesium sulphate, in presence of ammonia and ammonium chloride (the latter, to prevent precipitation of $Mg(OH)_2$ by the ammonia), white ppt. (crystalline in dilute solutions or on standing) of magnesium ammonium phosphate,

$$Na_2HPO_4 + MgSO_4 + NH_3 = Mg(NH_4)PO_4 + Na_2SO_4.$$

Silver nitrate, yellow ppt. of silver phosphate,

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3 *,$$

soluble in *acids* and in *ammonia*. [The above precipitation is therefore incomplete unless the free HNO_3 be neutralized.]

Ammonium molybdate $(NH_4)_2MoO_4$ in presence of strong HNO_3, on heating, canary yellow ppt. of ammonium phosphomolybdate. [Composition approximately

$$(NH_4)_3PO_4 . 12MoO_3,$$

but varies with conditions.]

The $(NH_4)_2MoO_4$ must be added considerably in excess of the phosphate taken.

Free orthophosphoric acid does not coagulate albumin.

Barium, strontium, lead, aluminium, bismuth, &c. salts give white ppts. of their respective normal or acid phosphates.

Metaphosphates.

Solution of metaphosphates (*e.g.* $NaPO_3$) give with

Silver nitrate, white ppt. of silver metaphosphate $AgPO_3$.

Magnesium sulphate, in presence of NH_3 and NH_4Cl, no ppt.

The free acid (or a metaphosphate + acetic acid) coagulates albumin.

Pyrophosphates.

Solutions of pyrophosphates (*e.g.* $Na_4P_2O_7$) give with

Silver nitrate, white ppt. of silver pyrophosphate $Ag_4P_2O_7$.

Magnesium sulphate, white ppt. of magnesium pyrophosphate $Mg_2P_2O_7$, soluble in excess.

The free acid does not coagulate albumin.

Boiled with water, in presence of acids, both meta and pyro-phosphates are converted into orthophosphates.

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* Although this equation, commonly given, represents roughly the general character of the change, the actual state of equilibrium reached depends on the proportions and concentration. The precipitate for example may contain Ag_2HPO_4 and $NaAgHPO_4$ as well as Ag_3PO_4, and the solution may contain NaH_2PO_4 as well as free phosphoric and nitric acids.

ARSENATES.

Solutions of arsenates (*e.g.* Na_2HAsO_4) give reactions similar to those of phosphates with ferric chloride, magnesium sulphate, and ammonium molybdate. Silver nitrate, however, gives, in neutral solution, a brick-red ppt. instead of yellow.

Arsenates are also distinguished (and separated) from phosphates by *hydrosulphuric acid* in presence of HCl, which gives first a white ppt. of sulphur, and afterwards a yellow ppt. of arsenious sulphide, on heating. [See Arsenic.]

BORATES.

(*E.g.* $Na_2B_4O_7$.)* Mixed with strong H_2SO_4 and alcohol, the latter on being kindled burns with a green-edged flame, owing to the presence of vapours of ethyl borate.

Solutions of borates *acidified* with dilute HCl, colour turmeric paper orange or brown (in dilute solutions only on drying). This colour is changed to green or blackish by treatment with KHO.

Solutions of borates give with *calcium chloride*, *barium chloride*, or *silver nitrate*, white ppts. (such as $2CaO.H_2O.3B_2O_3$, $BaBO_2$, $AgBO_2$, but variable in composition according to relative proportions used, temperature, &c.), readily soluble in dilute acids.

Strong hydrochloric acid gives white crystalline ppt. of boric acid, in concentrated solutions

$$Na_2O.2B_2O_3 + 2HCl + 5H_2O = 2(B_2O_3.3H_2O) + 2NaCl.$$

Free boric acid is volatile with steam

Borates undergo hydrolysis to a considerable extent when dissolved in water, so that the solutions react alkaline. For this reason, very dilute solutions of borates give a brown ppt. with silver nitrate.

$$NaBO_2 + HOH = NaOH + HBO_2$$
$$[\text{or } BO_2' + HOH = HBO_2 + OH'].$$

SILICATES.

Insoluble in water, except those of K and Na.

Silica, or insoluble silicates, when fused with excess of K_2CO_3 or Na_2CO_3 in a platinum vessel, give silicates which are soluble in water, *e.g.*

$$SiO_2 + K_2CO_3 = SiO_2.K_2O + CO_2.$$

* The boric acids known are $B(OH)_3$ [or $B_2O_3 3H_2O$] ortho; HBO_2 [or $B_2O_3.H_2O$] meta; and $H_2B_4O_7$ [or $H_2O.2B_2O_3$] 'pyro' or 'tetra.' No definite metallic salts corresponding to the ortho acid appear to have been isolated, but the esters are known. These three boric acids behave the same in solution, giving no distinguishing tests like the phosphoric acids.

Silicates (*continued*).

These, when dissolved in water and poured into an excess of HCl, give a solution containing silicic acid*,

$$SiO_2 . K_2O + 2HCl = SiO_2 . H_2O + 2KCl.$$

A solution of silicic acid, or a solution of any soluble silicate in HCl, when evaporated to dryness, leaves a residue of SiO_2, which is insoluble in all acids except HF.

Silica or silicates treated with a fluoride (*e.g.* NH_4F, or CaF_2) and concentrated H_2SO_4 give off gaseous silicon tetrafluoride,

$$SiO_2 + 2H_2SO_4 + 4NH_4F = 2(NH_4)_2SO_4 + SiF_4 + 2H_2O.$$

Solutions of silicates (*e.g.* K_2SiO_3) give white ppts. with calcium chloride, barium chloride, or silver nitrate, of variable composition; easily decomposed by acids.

CARBONATES.

(*E.g.* Na_2CO_3.) Treated with acids (either dilute or strong) CO_2 is evolved,

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$

This gas, when passed into lime water, gives white ppt. of calcium carbonate,

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O.$$

Excess of CO_2 redissolves the ppt.

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2.$$

On boiling, the resulting solution $CaCO_3$ is again precipitated.

Solutions of carbonates give with

Calcium chloride, white ppt. of calcium carbonate,

$$Na_2CO_3 + CaCl_2 = CaCO_3 + 2NaCl,$$

easily soluble in acids with effervescence.

Salts of almost all other metals give precipitates of carbonates, basic carbonates, or hydroxides.

Silver nitrate, yellowish-white ppt. of silver carbonate.

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* The silicic acids are perhaps best represented by the formulæ $x SiO_2 . y H_2O$. Metasilicic acid $SiO_2 . H_2O$ and orthosilicic acid $SiO_2 . 2H_2O$ can be obtained under certain conditions of drying; but there is little evidence to show their state of hydration when first separated. The composition of the silicates also is extremely variable, *e.g.* $x Na_2O . y SiO_2$. In the equations here given the coefficients x and y are omitted.

TARTRATES.

Solid tartrates heated with concentrated H_2SO_4 blacken immediately, owing to separation of carbonaceous matter, and evolve CO and CO_2.

Solutions of neutral tartrates, *e.g.* $KNa\overline{T} = \begin{array}{l} COOK \\ \dot{C}HOH \\ \dot{C}HOH \\ \dot{C}OONa \end{array}$, give with

Calcium chloride, in excess, white gelatinous ppt. of calcium tartrate,

$$KNa\overline{T} + CaCl_2 = Ca\overline{T} + KCl + NaCl,$$

soluble in HCl, HNO_3, and acetic acid*. Soluble also in cold NaHO (after washing), repptd. by boiling. Neutral cupric chloride converts it into *insoluble* cupric tartrate.

Potassium acetate, in presence of *acetic acid*, white crystalline ppt. of potassium hydrogen tartrate, especially on shaking,

$$Na_2T + CH_3COOK + CH_3COOH = KH\overline{T} + 2CH_3COONa,$$

more complete in presence of alcohol. Soluble in KOH, forming normal tartrate $K_2\overline{T}$.

Silver nitrate, white ppt. of silver tartrate,

$$KNa\overline{T} + 2AgNO_3 = Ag_2\overline{T} + KNO_3 + NaNO_3,$$

soluble in HNO_3 and in NH_3.

If dissolved in the least possible quantity of NH_3, the solution on heating deposits a bright mirror of metallic silver on the side of the tube†.

Potassium permanganate (one or two drops), in presence of caustic potash, is reduced on heating, first to green manganate,

$$2(K_2O \,.\, Mn_2O_7) + 4KOH = 4(K_2O \,.\, MnO_3) + 2H_2O + O_2,$$

which is rapidly changed to a brown ppt. of hydrated manganese dioxide,

$$2(K_2OMnO_3) + 4H_2O = 2(MnO_2 \,.\, H_2O) + 4KOH + O_2,$$

the tartrate being oxidised to formate carbonate, &c.

If to a neutral or acid solution of a tartrate (or tartaric acid), a little *ferrous sulphate* is added, followed by a few drops of *hydrogen dioxide*, and lastly excess of *caustic soda*, a deep violet or blue colour is obtained. (Metals other than K, Na, and NH_4, should be absent.) The colour is due to the formation of dihydroxymaleic acid, and reaction of this with ferric salt present; if a little ferric chloride is added the colour becomes more intense.

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* After standing some time calcium tartrate usually becomes crystalline, and will not then dissolve in acetic acid. The precipitation of calcium tartrate is retarded by the presence of ammonium chloride.

† The safest method of trying the "mirror" test is as follows: 1st, add *dilute* NH_3 to $AgNO_3$ till the ppt. first formed is *nearly* redissolved. 2nd, make the solution to be tested neutral or faintly alkaline with KOH. Mix the two solutions and heat gently.

CITRATES.

Solid citrates treated with concentrated H_2SO_4, evolve CO, and on heating blacken slowly, evolving CO_2, acetone, &c.

Solutions of normal citrates (*e.g.* $Na_3\overline{Ci}$ ($= C_3H_4(OH)(COONa)_3$)) give with

Calcium chloride, white ppt. of calcium citrate,

$$2Na_3\overline{Ci} + 3CaCl_2 = Ca_3\overline{Ci}_2 + 6NaCl,$$

soluble in dilute acids, and in *neutral cupric chloride.* Insoluble in cold KOH.

N.B. In the cold this precipitate may not appear for some hours, if the solutions are neutral, but it is formed in a few minutes if the solution is boiled, or immediately if NaOH is added.

Barium acetate, white ppt. of barium citrate $Ba_3\overline{Ci}_2$, especially in presence of alcohol and on long standing. (Tartaric acid, if present, must be first removed.)

Potassium permanganate, in presence of excess of KOH, is reduced on heating to green manganate, but is *not* further reduced, except after continued boiling.

Lime water added to *free* citric acid gives no ppt. (or only slight turbidity) in the cold, but on boiling, white calcium citrate is pptd.

Potassium acetate, no ppt. $AgNO_3$, white ppt. of $Ag_3\overline{Ci}$, which does not behave as with tartrate on dissolving in NH_3 and heating.

$FeSO_4$, H_2O_2, and NaOH, as above, gives only a yellow or brown colour.

CHLORIDES.

(*E.g.* NaCl.) Solid chlorides treated with concentrated H_2SO_4, evolve *hydrochloric acid* in the cold,

$$NaCl + H_2SO_4 = NaHSO_4 + HCl,$$

colourless gas forming dense white fumes of NH_4Cl on coming in contact with NH_3.

Heated with *manganese dioxide* and strong H_2SO_4, *chlorine* is evolved,

$$2NaCl + 2H_2SO_4 + MnO_2 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2,$$

yellowish-green gas, bleaches litmus, liberates I from KI.

Distilled with dry *potassium dichromate* and concentrated H_2SO_4, chromyl dichloride ("chlorochromic acid") is obtained,

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 = K_2SO_4 + 2Na_2SO_4 + 2CrO_2Cl_2 + 3H_2O,$$

orange red gas condensing to a deep red liquid; decomposed on coming in contact with water, giving chromic and hydrochloric acids,

$$CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

Silver and mercury chlorides give the above tests incompletely or not at all

Chlorides (*continued.*)

Solutions of chlorides give with

Silver nitrate, white ppt. of silver chloride which coagulates on shaking,

$$NaCl + AgNO_3 = AgCl + NaNO_3,$$

insoluble in HNO_3, soluble in NH_3. Turns violet on exposure to sunlight. Not decomposed on heating.

Lead acetate, white ppt. of lead chloride $PbCl_2$.

Mercurous nitrate, white ppt. of mercurous chloride HgCl.

HYPOCHLORITES.

(*E.g.* NaClO.) Treated with HCl, chlorine is evolved in the cold,

$$NaClO + HCl = NaCl + HClO,$$

and $$HClO + HCl = H_2O + Cl_2.$$

Solutions of hypochlorites bleach litmus, indigo, ink, &c.; when boiled they give chlorates and chlorides. They give with

Manganous chloride, brown ppt. of hydrated manganese dioxide, or intermediate oxide $x\,MnO_2 . y\,MnO$,

$$NaClO + MnCl_2 + 2NaOH = MnO_2 . H_2O + 3NaCl.$$

Metallic mercury, on shaking, yellow deposit of mercuric oxide,

$$NaClO + Hg = NaCl + HgO.$$

Free hypochlorous acid shaken with metallic mercury gives yellow or brown mercuric oxychloride, $HgCl_2 . x\,HgO$; whereas free chlorine gives white mercurous chloride, HgCl.

Silver nitrate gives silver chloride and chlorate; solutions of hypochlorites, however, nearly always contain chloride and free alkali, which also act on the silver nitrate.

CHLORATES.

(*E.g.* $KClO_3$.) Treated with concentrated H_2SO_4, the liquid turns yellow, and on heating, chlorine peroxide (yellow explosive gas) is evolved,

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + 2ClO_2.$$

Heated with strong HCl, chlorine peroxide and chlorine are evolved.

Most chlorates, when heated alone to redness, evolve oxygen and leave a chloride,

$$2KClO_3 = KClO_4 + KCl + O_2,$$

and at higher temperature, $$KClO_4 = KCl + 2O_2.$$

Chlorates in solution are reduced to chlorides by zinc or by ferrous salts and dilute acid.

Solutions of chlorates acidulated with dilute H_2SO_4 bleach indigo only *on heating*. If a few drops of *sulphurous acid* be added, however, they do so *in the cold* (the chlorate being reduced to chlorite or hypochlorite).

PERCHLORATES.

(*E.g.* $KClO_4$.) Treated with concentrated H_2SO_4 gives no ClO_2; only the free acid distils.

Perchlorates are not reduced by zinc or by sulphurous acid. Free perchloric acid gives with potassium salts a crystalline ppt. of $KClO_4$.

IODIDES.

(*E.g.* KI.) Treated with concentrated H_2SO_4, iodine is liberated as a brown or black ppt. which, on heating, gives violet vapours,

$$2KI + 3H_2SO_4 = 2KHSO_4 + SO_2 + 2H_2O + I_2.$$

Free iodine colours starch-paste blue; the colour is temporarily destroyed by heat.

Solutions of iodides give with

Silver nitrate, pale yellow ppt. of silver iodide,

$$KI + AgNO_3 = AgI + KNO_3,$$

practically insoluble in ammonia. Insoluble in dilute HNO_3. Darkens on exposure to light.

Chlorine water, *nitrous acid*, or other oxidising agents, liberate iodine,

$$2KI + Cl_2 = 2KCl + I_2$$

$$2HI + 2HNO_2 = 2H_2O + 2NO + I_2.$$

If the mixture be shaken up with carbon disulphide, the iodine is dissolved out, giving a violet colour. Excess of chlorine water destroys the colour, converting the free iodine into iodic acid.

Cupric sulphate, dirty white ppt. of cuprous iodide, with liberation of iodine,

$$4KI + 2CuSO_4 = 2CuI + 2K_2SO_4 + I_2.$$

Cupric iodide is probably first formed and decomposes (not completely) into cuprous iodide and iodine.

In presence of sulphurous acid no iodine is liberated,

$$2KI + 2CuSO_4 + H_2SO_3 + H_2O = 2CuI + 2KHSO_4 + H_2SO_4.$$

Lead acetate, yellow ppt. of lead iodide PbI_2, soluble in boiling water, crystallizing out on cooling.

Mercuric chloride, red ppt. of mercuric iodide HgI_2, soluble in KI and in $HgCl_2$.

Palladium nitrate, black ppt. of PdI_2.

IODATES.

(*E.g.* KIO_3 (or $K_2I_2O_6$)*.) Boiled with strong HCl, chlorine is evolved, together with iodine trichloride,

$$KIO_3 + 6HCl = KCl + 3H_2O + ICl_3 + Cl_2.$$

Strong H_2SO_4 liberates iodic acid, but no free iodine.

Solutions of iodates give with

Potassium iodide, in presence of a dilute acid (H_2SO_4, HCl, or CH_3COOH), liberation of iodine,

$$5HI + HIO_3 = 3H_2O + 3I_2.$$

Silver nitrate, white ppt. of silver iodate,

$$KIO_3 + AgNO_3 = AgIO_3 + KNO_3,$$

sparingly soluble in cold dilute HNO_3. Easily soluble in ammonia, from which solution, SO_2 precipitates AgI, insoluble in ammonia.

Barium chloride, white crystalline ppt. of barium iodate $BaI_2O_6 . H_2O$.

Pyrogallol $C_6H_3(OH)_3$, brownish-red colour, sometimes ppt. of purpurogallin $C_{20}H_{16}O_9$.

BROMIDES.

(*E.g.* KBr.) Heated with concentrated H_2SO_4, bromine is evolved, mixed with hydrobromic acid,

$$KBr + H_2SO_4 = KHSO_4 + HBr$$

$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2.$$

Free bromine colours starch-paste yellow.

Heated with concentrated H_2SO_4 and manganese dioxide, bromine alone is evolved,

$$2KBr + 3H_2SO_4 + MnO_2 = 2KHSO_4 + MnSO_4 + 2H_2O + Br_2.$$

Solutions of bromides give with

Silver nitrate, yellowish-white ppt. of silver bromide,

$$KBr + AgNO_3 = AgBr + KNO_3,$$

sparingly soluble in ammonia. Insoluble in dilute HNO_3. Darkens on exposure to sunlight.

Chlorine water liberates free bromine,

$$2KBr + Cl_2 = 2KCl + Br_2.$$

If the mixture be shaken up with carbon disulphide, the bromine is dissolved out, giving a yellow or orange colour.

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* Although the single formula KIO_3 is commonly used, there are some reasons for considering that iodic acid is dibasic, and has the formula $H_2I_2O_6$, *e.g.* it yields an anhydride by simply heating, and gives more than one potassium salt. The behaviour of iodic acid in solution also indicates the existence of more complex forms, except at great dilution.

BROMATES.

(*E.g.* $KBrO_3$.) Heated with acids, bromic acid, $HBrO_3$, is liberated, which soon decomposes, giving off bromine and oxygen,

$$4HBrO_3 = 2H_2O + 2Br_2 + 5O_2.$$

Solutions of bromates give with

Silver nitrate, white ppt. of silver bromate,

$$KBrO_3 + AgNO_3 = AgBrO_3 + KNO_3,$$

sparingly soluble in dilute HNO_3. Soluble in ammonia.

Potassium bromide, in presence of cold dilute acid, causes liberation of bromine,

$$HBrO_3 + 5HBr = 3H_2O + 3Br_2.$$

CYANIDES.

Treated with dilute HCl or other dilute acids, many cyanides (*e.g.* KCN, or $Zn(CN)_2$) evolve hydrocyanic acid in the cold; others (*e.g.* $Hg(CN)_2$, or AgCN) require strong HCl and heating.

$$KCN + HCl = KCl + HCN.$$

The evolved HCN may be absorbed by KOH (on a watch-glass or filter paper) and tested with iron salts as below; or by $(NH_4)_2S_2$, and tested for *sulphocyanate* with HCl and $FeCl_3$—[$(NH_4)_2S_2 + HCN = NH_4CNS + NH_4HS$)].

Heated with excess of concentrated H_2SO_4, carbon monoxide is evolved (in part),

$$2KCN + 4H_2SO_4 + 2H_2O = 2KHSO_4 + 2NH_4HSO_4 + 2CO.$$

Solutions of cyanides (not mercuric cyanide*) give with

Silver nitrate, white ppt. of silver cyanide,

$$KCN + AgNO_3 = AgCN + KNO_3,$$

insoluble in cold dilute HNO_3; easily soluble in ammonia, and in KCN. Not darkened by exposure to sunlight. On heating, it decomposes into metallic silver, cyanogen, and paracyanogen. Decomposed by strong HCl, giving silver chloride.

On adding successively *ferrous sulphate*, *ferric chloride*, and *hydrochloric acid*, a dark blue ppt., "Prussian blue," is obtained,

$$6KCN + FeSO_4 = K_4FeC_6N_6 + K_2SO_4$$

$$3K_4FeC_6N_6 + 4FeCl_3 = Fe_4(FeC_6N_6)_3† + 12KCl.$$

(If the solution contains free acid to start with, NaOH must be added before applying the test. The object of the HCl is to dissolve the hydroxides of iron which are precipitated by alkali present.)

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* Mercuric cyanide behaves abnormally, being a non-electrolyte; it gives no ppt. with $AgNO_3$ and does not yield the Prussian blue test. HCl or H_2S however decomposes it with evolution of HCN.

† See Ferric Salts.

CYANATES.

(*E.g.* KCNO.) Treated with dilute acids, carbon dioxide is evolved, and an ammonium salt formed, which may be identified as usual,

$$KCNO + HCl = KCl + HCNO$$

$$HCNO + H_2O + HCl = NH_4Cl + CO_2.$$

Traces of HCNO escape undecomposed, giving a pungent odour.

Solutions of cyanates treated with ammonium sulphate give ammonium cyanate, by double decomposition, which is soon transformed into urea,

$$NH_4CNO = CO(NH_2)_2.$$

The solution may be evaporated to dryness (on a water bath), the urea extracted with alcohol, and identified as usual.

Silver nitrate gives white ppt. of silver cyanate AgCNO, easily soluble in ammonia. Decomposed by acids as above.

Cobalt acetate gives a blue colour due to $K_2[Co(CNO)_4]$, which behaves on dilution, &c., in the same way as the sulphocyanate compound (see page 19). Cyanides must be absent.

FERROCYANIDES.

(*E.g.* $K_4FeC_6N_6$.) Heated with strong H_2SO_4, carbon monoxide is evolved,

$$K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO.$$

With dilute H_2SO_4, hydrocyanic acid is obtained,

$$2K_4FeC_6N_6 + 3H_2SO_4 = K_2Fe(FeC_6N_6) + 3K_2SO_4 + 6HCN.$$

Solutions of ferrocyanides give with

Silver nitrate, white ppt. of silver ferrocyanide,

$$K_4(FeC_6N_6) + 4AgNO_3 = Ag_4(FeC_6N_6) + 4KNO_3,$$

insoluble in dilute HNO_3 and in cold ammonia.

Ferric chloride, dark blue ppt. of "Prussian blue." (See Ferric salts.)

Ferrous sulphate, pale blue (white if quite pure) ppt. of potassium ferrous ferrocyanide,

$$K_4FeCy_6 + FeSO_4 = K_2Fe''FeCy_6 + K_2SO_4.$$

Cupric sulphate in excess, chocolate ppt. of cupric ferrocyanide,

$$K_4FeC_6N_6 + 2CuSO_4 = Cu_2(FeC_6N_6) + 2K_2SO_4.$$

Oxidising agents, such as $KMnO_4$ or chlorine, convert ferrocyanides into ferricyanides,

$$10K_4FeC_6N_6 + K_2O \,.\, 2MnO \,.\, O_5 + 8H_2SO_4 = 10K_3(FeC_6N_6) + 6K_2SO_4 + 2MnSO_4 + 8H_2O.$$

FERRICYANIDES

(*E.g.* $K_3FeC_6N_6$.) Heated with concentrated H_2SO_4, carbon monoxide is evolved (also CO_2, &c.) and ferric, potassium, and ammonium sulphates remain.

Solutions of ferricyanides give with

Silver nitrate, orange ppt. of silver ferricyanide,

$$K_3FeC_6N_6 + 3AgNO_3 = Ag_3FeC_6N_6 + 6KNO_3,$$

insoluble in dilute HNO_3, soluble in ammonia.

Ferrous sulphate, dark blue ppt. of "Turnbull's blue." (See page 11.)

Potassium iodide (in presence of HCl) reduces ferri- to ferro-cyanides with liberation of iodine,

$$2K_3FeC_6N_6 + 2KI = 2K_4FeC_6N_6 + I_2.$$

Ferric chloride, no ppt. (brown solution, green if not quite pure).

Copper sulphate, yellowish-green ppt., *Nickel sulphate,* yellowish-green ppt.
Cobalt nitrate, reddish-brown ppt. of the respective ferricyanides.

SULPHOCYANATES
or Thiocyanates.

(*E.g.* KCNS.) Heated with strong HCl or H_2SO_4, carbon oxysulphide, carbon dioxide, hydrosulphuric acid, hydrocyanic acid, &c., are evolved,

$$KCNS + H_2SO_4 = KHSO_4 + HCNS$$

$$3HCNS = \underset{\text{(yellow ppt.)}}{H_2C_2N_2S_3} + HCN$$

$$HCNS + 2H_2O = CO_2 + H_2S + NH_3.$$

Solutions of sulphocyanates give with

Ferric chloride, blood-red colour due to ferric sulphocyanate $Fe(CNS)_3$, soluble in ether. The colour is bleached by mercuric chloride, but not by dilute HCl.

Silver nitrate, white ppt. of silver sulphocyanate,

$$KCNS + AgNO_3 = AgCNS + KNO_3,$$

easily soluble in ammonia, insoluble in dilute HNO_3.

Copper sulphate, in presence of SO_2 white ppt. of cuprous sulphocyanate.
Cobalt nitrate, blue colour, destroyed by dilution. (See page 20.)

NITRATES.

(*E.g.* KNO_3.) Heated with concentrated H_2SO_4, nitric acid is evolved,

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

Part of the HNO_3 usually splits up, giving yellow or brown vapours of lower nitrogen oxides, *e.g.*

$$4HNO_3 = 2H_2O + 4NO_2 + O_2.$$

Heated with concentrated H_2SO_4 and metallic copper, brownish-red fumes of nitrogen peroxide are given off,

$$2KNO_3 + 3H_2SO_4 + Cu = 2KHSO_4 + CuSO_4 + 2H_2O + 2NO_2.$$

Solutions of nitrates

Treated with excess of *ferrous sulphate* in the cold, and concentrated H_2SO_4 gradually poured in down the side of the tube, give a brown ring where the liquids meet,

$$2KNO_3 + 6FeSO_4 + 4H_2SO_4 = K_2SO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

and

$$FeSO_4 + NO = \underbrace{xFeSO_4\,yNO}_{\text{brown compound}}.$$

This brown solution probably contains the complex ion $(FeNO)''$. Heat destroys the colour, NO being evolved.

Treated with zinc and a little acetic acid they are reduced (in part at any rate) to nitrites,

$$KNO_3 + H_2 = KNO_2 + H_2O,$$

which may be detected by the KI + HCl test, &c. [See Nitrites.]

It is best to mix the nitrate solution with KI, and then add the acid and zinc.

Brucine in presence of concentrated H_2SO_4 gives a red colour*.

Mixed with dilute H_2SO_4, solutions of nitrates do not bleach *indigo* in the cold (even in presence of SO_2), but do so on heating.

Boiled with *zinc* and *caustic soda* they give off ammonia,

$$NaNO_3 + 4Zn + 7NaOH = 4Zn(ONa)_2 + 2H_2O + NH_3.$$

'*Nitron*' even in very dilute solutions gives a colourless crystalline precipitate; see page [illegible]

NITRITES.

(*E.g.* KNO_2.) Treated with dilute acids, nitric oxide is evolved,

$$KNO_2 + HCl = KCl + HNO_2$$

and

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

The evolved gas unites with oxygen from t[illegible] giving brownish-red fumes of N_2O_4.

Solutions of nitrites give with

Ferrous sulphate, even in neutral solu[illegible] presence of *dilute* acid, a brown colour,

$$2KNO_2 + 2FeSO_4 + 2H_2SO_4 [illegible] K_2SO_4 + Fe_2(SO_4)_3 + 2H_2O + 2NO.$$

The resulting NO reacts with more $FeSO_4$, giving the brown colour. [Compare Nitrates.]

* Chlorates, and under certain conditions, nitrites, give a similar colour.

Nitrites (*continued*).

Potassium iodide, in presence of dilute HCl or H_2SO_4, liberation of iodine (detected by starch-paste or CS_2),

$$2KNO_2 + 2KI + 4HCl = 4KCl + 2H_2O + 2NO + I_2.$$

Urea, added to free nitrous acid (or a nitrite + dilute H_2SO_4), gives off nitrogen and carbon dioxide,

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 3H_2O + 2N_2$$

(complete on heating).

Boiled with *zinc* and *caustic soda* they behave like nitrates, ammonia being evolved.

Silver nitrate, white ppt. of silver nitrite, soluble in hot water.

Potassium permanganate, in presence of dilute H_2SO_4, is at once discolorized.

Meta-diamino-benzene $C_6H_4(NH_2)_2$ in presence of dilute H_2SO_4, a yellow colour, even in very dilute solutions.

Aniline sulphate (one or two drops of solution) triturated with a concentrated solution of a nitrite gives the odour of phenol C_6H_5OH.

If quite free from nitrates, it is stated that nitrites when mixed with concentrated H_2SO_4 (so as to form nitrosyl-sulphuric acid) do not give a red colour with brucine; this is true if certain conditions are fulfilled.

ACETATES.

(*E.g.* $CH_3.COONa$.) Heated with concentrated H_2SO_4, acetic acid is given off (recognized by its odour),

$$CH_3.COONa + H_2SO_4 = NaHSO_4 + CH_3.COOH.$$

Heated with concentrated H_2SO_4 and *alcohol* (one or two drops) the characteristic odour of ethyl acetate is produced,

$$CH_3.COOH + (C_2H_5)OH = CH_3.COO(C_2H_5) + H_2O.$$

Heated with arsenious anhydride, characteristic (poisonous) odour of cacodyl oxide $As_2(CH_3)_4O$ is produced.

Neutral solutions of acetates give with

Ferric chloride, a red colour, due to ferric acetate $Fe(CH_3CO_2)_3$. On boiling the solution, a brown ppt. is produced of basic ferric acetate $Fe(CH_3CO_2)_3\,x Fe(OH)_3$. The red colour is bleached by HCl but not by $HgCl_2$.

Silver nitrate gives, in strong solutions, white ppt. of silver acetate, soluble in hot water.

FORMATES.

(*E.g.* H . COONa.) Heated with concentrated H_2SO_4, carbon monoxide is evolved without blackening of the liquid,

$$H.COONa + H_2SO_4 = NaHSO_4 + H_2O + CO.$$

Heated with alcohol and a small quantity of concentrated sulphuric acid, ethyl formate, having a pungent characteristic odour, is produced.

Neutral solutions of formates give with

Silver nitrate, on heating, a black ppt. of metallic silver. A white ppt. is first produced in the cold if the solution is concentrated.

Mercurous nitrate, white ppt. of mercurous formate, quickly turning grey owing to reduction to mercury.

Ferric chloride gives a reaction similar to that produced with acetates.

ANALYTICAL TABLES.

The Tables for Systematic Analysis will be found on page 50 and the following pages: Tables A and B which precede them are intended for beginners only.

INTRODUCTORY TABLES FOR THE ANALYSIS OF A SIMPLE SALT IN THE WET WAY. FOR BEGINNERS. A. EXAMINATION FOR ONE METAL.

These tables have been introduced for the sake of students who are attempting Qualitative Analysis for the first time. The scheme is by no means intended to be a complete one, and will only serve for the simplest cases. For complete and systematic analysis, the Tables commencing on page 50 must be employed.

Preparation of the original solution*. Dissolve the salt in water if possible. If it does not dissolve, even on boiling, try dilute hydrochloric acid; this failing, try strong hydrochloric acid, dilute nitric acid, strong nitric acid and aqua regia, in the order named. If still insoluble the substance must be treated by special methods (page 52).

Test portions of the original solution as follows, in the order mentioned, until the metal is found.

I.

Add dilute ***hydrochloric acid*** drop by drop. [If this acid has been used in dissolving the salt, the test is of course unnecessary.]

If a white precipitate is produced, which does not redissolve on further addition of the acid, the metal present is either silver, lead or mercury (mercurous). [If the precipitate readily redissolves in excess of the acid and again appears on adding much water, antimony or bismuth is indicated. If the acid used is too strong, barium salts may be precipitated, but these will dissolve in water.]

Shake the mixture well, pour off clear liquid, wash precipitate with cold water and shake it with *ammonia*. The precipitate dissolves, **Silver**; turns black, **Mercury** (mercurous); remains white and insoluble, **Lead.** [In very dilute solutions lead is only found in II.]

II.

[If nitric acid or strong hydrochloric acid has been used to dissolve the substance, the solution must be largely diluted before this test is applied. If aqua regia has been used, the solution must be well boiled and diluted.]

Add a little dilute hydrochloric acid (if necessary) and pass ***hydrosulphuric acid*** gas to saturation. If no precipitate appears, or if the precipitate is white and does not settle, boil the solution and again pass the gas.

A precipitate indicates Arsenic (*bright yellow*), Antimony (*orange*), Tin (stannic) (*dull yellow*), Cadmium (*lemon yellow*), Tin (stannous) (*dark brown*), Mercury (*black*), Lead (*black*), Copper (*dark brown or black*), Bismuth (*dark brown or black*)†. Filter off the precipitate, wash it and digest a portion of it with warm (yellow) *ammonium sulphide.*

(A) *The precipitate dissolves.* The metal is arsenic, antimony or tin. Digest another portion of the precipitate with ammonium carbonate; if it dissolves entirely, the metal is **Arsenic**‡; if it is insoluble, or nearly so, test the original solution for antimony and tin by pouring a few drops of it, acidified with hydrochloric acid, on to a piece of zinc in contact with platinum foil; a black stain on the platinum indicates **Antimony.** Detach the remaining zinc from the platinum and dissolve it completely in strong hydrochloric acid; cool and add mercuric chloride; a white or grey precipitate indicates **Tin.** [*Test original solution with mercuric chloride to ascertain whether stannous or stannic.* See page 10.]

(B) *The precipitate does not dissolve.* To a portion of the original solution add *caustic soda*; yellow precipitate indicates **Mercury** (mercuric), a blue precipitate, **Copper**; the other metals mentioned give white precipitates. Test portions of the original solution as follows:—(*a*) Add ammonia, dissolve the resulting white precipitate in a very little hydrochloric acid and add much *water*; a white precipitate indicates **Bismuth.** (*b*) Add *dilute sulphuric acid*; white precipitate indicates **Lead.** (*c*) Add potassium cyanide, until the precipitate produced is redissolved, and pass *hydrosulphuric acid*; yellow precipitate indicates **Cadmium.**

III.

Add a drop or two of nitric acid and heat; if any marked change is observed, add more of the acid until no further effect is produced.

Add ammonium chloride in excess and ***ammonia*** till alkaline; boil. A precipitate indicates Iron (*reddish-brown*), Chromium (*green*) or Aluminium (*white, gelatinous*). [*Also certain phosphates, oxalates, etc., which dissolve in acids but are precipitated by ammonia; for these, see complete Tables.*]

Test a portion of the original solution with *caustic soda*; a precipitate which is

Reddish-brown indicates **Iron** (ferric). [Confirm in original solution by potassium ferrocyanide; dark blue precipitate.]

Green, turning brown in the air, **Iron** (*ferrous*). [Confirm in original solution by potassium ferricyanide; dark blue precipitate.]

Bluish-green, soluble in excess to green solution, **Chromium.** [Confirm by adding a little hydrogen dioxide to the green solution in caustic soda, and boiling; solution turns yellow.]

White, soluble in excess, **Aluminium.**

[*White, insoluble in excess,* the phosphates, etc. referred to above.]

IV.

Add ammonium chloride in excess, ammonia till alkaline and ***ammonium sulphide.*** A precipitate indicates Nickel (*black*), Cobalt (*black*), Zinc (*white, often discoloured*) or Manganese (*buff or pink*). Test a portion of the original solution with *caustic soda.*

A precipitate which is *blue, insoluble in excess,* indicates **Cobalt.** *Apple-green, insoluble in excess,* **Nickel.** *White, insoluble in excess, but turning brown in the air,* **Manganese.** *White, soluble in excess,* **Zinc.**

V.

Add ammonium chloride in excess, ammonia till alkaline and ***ammonium carbonate.*** A white precipitate indicates Barium, Strontium or Calcium. Test a portion of the original solution with *calcium sulphate*; immediate white precipitate, **Barium**; white precipitate on standing or warming, **Strontium.** If no precipitate, confirm **Calcium** in original solution by adding ammonia and *ammonium oxalate*; white precipitate insoluble in acetic acid.

VI

Add ammonium chloride in excess, ammonia and ***sodium phosphate:*** a white precipitate indicates Magnesium. [In dilute solutions, this precipitate only appears on stirring or standing.]

VII.

Test original substance for **Ammonium** by boiling it with caustic soda and recognising the evolved ammonia by its action on red litmus, odour, etc. If ammonium is absent, test for **Potassium** by adding *platinic chloride* to a few drops of the original solution, acidified with hydrochloric acid, on a watch glass; a yellow precipitate on stirring indicates potassium if ammonium is absent. **Sodium** is indicated if the original substance leaves a residue when heated to redness and gives a strong yellow colour to the bunsen flame when heated on a platinum wire.

The results obtained should be confirmed by the dry tests (page 50) and by the general reactions (pages 1 to 24).

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* The solution must not be too strong; about 1 gram in 25 c.c. is usually sufficient.

† A white or yellowish precipitate which does not settle is probably sulphur produced from the hydrosulphuric acid and indicating therefore an oxidising agent (*e.g.* a ferric salt, chromate, hypochlorite, etc.). If sulphur is precipitated and the solution changes from orange to green, a chromate or bichromate is indicated.

‡ Arsenic is nearly always present as an arsenite or arsenate, and will be again looked for in the Table for Acids. If arsenic is found therefore, in a single salt, another metal must be sought for. Arsenates are sometimes overlooked in this Table owing to the fact that the precipitate produced by hydrosulphuric acid only comes down slowly, on boiling, after sulphur has separated.

INTRODUCTORY TABLES FOR THE ANALYSIS OF A SIMPLE SALT IN THE WET WAY. FOR BEGINNERS. B. EXAMINATION FOR ONE ACID RADICLE.

I. Treat the original substance (or aqueous solution) with *dilute Hydrochloric Acid*; afterwards heat.

Effervescence in the cold with evolution of *carbon dioxide* (recognised by turning lime-water milky)	indicates	**Carbonate.**
Evolution of *sulphur dioxide* (recognised by its odour and by its turning a solution of potassium bichromate green)	„	**Sulphite.**
„ „ *sulphur dioxide* with separation of yellow *sulphur*	„	**Thiosulphate.**
„ „ *hydrosulphuric acid* gas (recognised by its odour and by its turning lead acetate black)	„	**Sulphide.**
„ „ *chlorine* (recognised by its odour, colour and by its bleaching wet litmus paper)	„	**Hypochlorite.**
„ „ *hydrocyanic acid* (recognised by its odour and by confirmatory test mentioned below)	„	**Cyanide.**
„ „ *oxides of nitrogen* (reddish brown fumes)	„	Nitrite.

[*Some sulphides require heating with* STRONG *hydrochloric acid. Chlorates may evolve chlorine mixed with oxides of chlorine if the acid is sufficiently strong and sulphocyanates may give carbon dioxide and hydrosulphuric acid; they will be detected by the following tests.*]

II. Heat solid substance* with *strong sulphuric acid.*

Evolution of a yellow explosive gas (*chlorine dioxide*) and liquid turning yellow	indicates	**Chlorate.**
„ „ *iodine* (violet vapour which turns starch paste blue)	„	**Iodide.**
„ „ *bromine* (brownish red vapour which turns starch paste yellow)	„	**Bromide.**
„ „ *hydrochloric acid* (colourless gas which fumes in the air)	„	**Chloride.**
„ „ *carbon monoxide* (colourless gas which burns with a blue flame on ignition) ...	„	**Oxalate** or **Ferrocyanide** (Cyanide or Ferricyanide).
„ „ „ „ with separation of black carbonaceous matter	„	**Tartrate** (or Citrate).
„ „ *nitric acid* (pungent acid fumes usually mixed with reddish brown oxides of nitrogen)	„	**Nitrate.**
„ „ *hydrofluoric acid* (pungent acid fumes which (owing to action on test tube) give a white deposit on a wet rod)	„	**Fluoride.**
„ „ *acetic acid* (recognised by its odour and by special tests below)	„	**Acetate.**

III. Dissolve original salt in water (or in acids, as directed in Table A). Acidify with dilute hydrochloric acid (filter if necessary) and add ***barium chloride.*** White precipitate indicates **Sulphate.** [Silicofluorides also form a precipitate; to distinguish, test original solution with strontium nitrate which precipitates sulphate but not silicofluoride.]

IV. Dissolve original salt in water (or in dilute *nitric* acid). Add dilute nitric acid and *silver nitrate*. A precipitate indicates chloride, cyanide, sulphocyanate or ferrocyanide (white); bromide (white or yellowish), iodide (yellow), [chromate (crimson) from strong solution], ferricyanide (orange). Shake, pour off clear liquid, wash precipitate and digest it with *ammonia*. Chloride, cyanide, ferricyanide dissolve easily, sulphocyanate less easily, bromide sparingly, iodide and ferrocyanide scarcely at all.

F.

V. To the original aqueous solution † add ammonia till just alkaline and ***calcium chloride.*** A white precipitate indicates carbonate, oxalate, fluoride, phosphate, arsenate, borate, tartrate, (citrate, ferrocyanide, silicate). Add excess of acetic acid; **oxalate** and **fluoride** are insoluble, the others dissolve (silicate decomposes, often with separation of silicic acid).

VI. To the original aqueous solution † (made *neutral* if necessary by a drop or two of ammonia or dilute hydrochloric acid) add ***ferric chloride.*** Dark blue precipitate indicates **Ferrocyanide.** Blood red colour indicates **Sulphocyanate** (bleached by mercuric chloride), **Acetate** (not bleached by mercuric chloride), or Iodide (gives violet colour to carbon disulphide). Yellowish white precipitate indicates *phosphate* or *arsenate*.

Many of the acid radicles will be detected with tolerable certainty by the above tests; the following distinguishing or confirmatory tests must however be tried in the original aqueous solution †.

Nitrate. Add *ferrous sulphate* and gradually pour in *strong sulphuric acid*, brown or pink ring where the liquids meet.

Chlorate. Add two or three drops of *sulphurous acid* and *indigo* solution, the latter is bleached; without sulphurous acid it is not bleached.

Hypochlorite. *Manganous chloride*, brown precipitate.

Chloride. Solid (or strong solution) heated with *manganese dioxide* and *sulphuric acid* evolves chlorine (detected as above).

Cyanide. Add *ferrous sulphate*, *ferric chloride* and *dilute sulphuric acid*, dark blue precipitate.

Tartrate. Add a drop of *ferrous sulphate*, two or three drops of *hydrogen dioxide* and excess of *caustic soda*; deep violet colour.

Arsenate. Carefully *neutralise* solution and add *silver nitrate*, brick-red precipitate. [**Arsenite** gives yellow, *Phosphate*, yellow, *Chromate* (and *bichromate*), crimson, *Sulphide*, black.]

Ferricyanide. *Ferrous sulphate*, dark blue precipitate.

Chromate (and *bichromate*). Boil with dilute hydrochloric acid and a few drops of alcohol; orange colour changes to green, and the resulting solution gives a bluish green precipitate with ammonia.

Phosphate. Add nitric acid and excess of *ammonium molybdate*; yellow precipitate on heating (Arsenate gives similar reaction).

Borate. Mix with strong sulphuric acid and alcohol in a dish; set fire to the alcohol, green flame.

Acetate. Solid heated with *strong sulphuric acid* and a few drops of *alcohol* gives odour of ethyl acetate.

Oxalate. Solid heated with concentrated sulphuric acid evolves carbon monoxide and carbon dioxide without blackening.

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* If the substance to be tested is given in solution it should be neutralised, if necessary, with sodium carbonate and evaporated just to dryness before applying this test.

† The presence of metals, other than potassium, sodium or ammonium, may often interfere with the tests for acids; hence, in the cases to which this reference is given, test a portion of the solution with sodium carbonate; if a precipitate is produced boil the original solid, or solution, with sodium carbonate, in sufficient excess, filter off precipitate, just acidify filtrate with dilute nitric acid, warm to expel carbon dioxide and carefully neutralise with ammonia. Use this solution for the tests referred to.

PRELIMINARY EXAMINATION OF SOLID IN THE DRY WAY.

	Experiment	Observation	Inference
1.	Heat on charcoal before the blow-pipe	Residue which is white and fusible (see also 5)	Alkali or alkaline earth
		,, ,, ,, ,, infusible (see 2, 3 and 5)	
		,, ,, yellow while hot, white when cold (see also 3)	Zn
		,, ,, black or coloured, or metal beads (see 2 and 4)	
		Volatilizes (see also 2, 6 and 7)	Hg, As, (NH_4), certain chlorides, organic acids, iodine, &c.
		Burns away	S, C, organic substances, &c.
		Deflagrates	Nitrates, Chlorates, &c.
2.	Mix substance with Na_2CO_3* and again heat on charcoal in reducing flame	Red malleable metallic spangles or globules (see 4 and 5)	Cu
		Metal beads which are malleable, with yellow incrustation	Pb
		,, ,, ,, without incrustation	Ag
		,, ,, ,, with slight incrustation, yellow when hot	Sn
		,, ,, brittle, with orange or yellow incrustation	Bi
		,, ,, ,, with white incrustation	Sb
		Brown incrustation	Cd
		Odour of garlic (see also 6)	As
		,, ammonia (see also 6)	NH_4
		Residue which when dissolved in water gives black stain on silver	Sulphur compounds
3.	Treat the white residue from 1 with cobalt nitrate and again heat	Blue mass	Al (possibly phosphates of Ca, &c.)
		Bright green mass	Zn
		Dirty bluish green mass	Sn
		Pale pink mass	Mg
4.	Heat *small* quantity of substance in a borax bead, first in reducing, afterwards in oxidising flame	Reducing flame — Oxidising flame	
		Green — Green	Cr‡
		Blue — Blue	Co
		(Red†) — Green hot, blue cold	Cu
		Colourless — Violet	Mn‡
		Grey — Brownish violet	Ni
		(Bottle green) — Reddish yellow hot, pale yellow cold	Fe
5.	Heat substance moistened with HCl, on a clean platinum wire in reducing flame (or edge of Bunsen flame	Flame is coloured Crimson	Sr
		,, ,, Green	Ba, HBO_2, Cu
		,, ,, Violet	K
		,, ,, Intense yellow	Na
		,, ,, Orange	Ca
		,, ,, Blue	As, Sb, Pb, &c.
6.	Heat in dry bulb tube with dry Na_2CO_3 and powdered charcoal	Black mirror, which when heated in open tube gives white crystalline deposit	As
		Grey sublimate uniting into globules when rubbed	Hg
		Odour of ammonia	NH_4

7. Heat substance in a narrow hard glass tube	Water is given off and condenses on colder parts of tube	Water of crystallisation or of hydration, acid-salts, organic compounds
	A white sublimate is formed	NH_4 salts, oxides of As or Sb, chlorides or bromides of Hg, many organic compounds
	A grey or black sublimate is formed	Hg, HgS, As
	A yellow sublimate is formed	S. Polysulphides. HgI_2 (turns red when rubbed)
	A black ,, ,, with violet vapours	Iodine, certain iodates and iodides
	A colourless gas is evolved which on examination proves to be—	
	O_2 detected by glowing splinter	Chlorates, hypochlorites, nitrates, peroxides, oxides of Hg and Ag
	N_2O§ ,, ,, ,, ,,	Ammonium nitrate
	CO_2 ,, ,, lime water	Carbonates, organic salts
	CO ,, ,, burning with blue flame when ignited	Oxalates and some other organic salts
	NH_3 ,, ,, odour, litmus, HCl fumes, &c.	NH_4 salts, urea, &c.
	SO_2 ,, ,, potassium bichromate	Acid sulphites, thiosulphates, some sulphates
	H_2S ,, ,, lead acetate	Hydrosulphides
	C_2N_2 ,, ,, burning with pink flame when ignited	Cyanides of Hg, Ag, Cu, Zn
	A coloured gas is evolved which on examination proves to be—	
	NO_2 reddish brown, detected by $FeSO_4$	Nitrates of heavy metals
	I_2 violet, detected by starch, &c.	Iodine, &c., as above
	Br_2 orange red, detected by starch, &c.	Certain bromides and bromates
	Cl_2 (yellowish green) detected by bleaching, KI, &c.	Certain chlorides, *e.g.* of Au, Pt, Cu"

8. Further information may usually be obtained by application of Bunsen's film-reactions. A small quantity of the substance is taken up on an asbestos thread and held in the upper reducing part of a small Bunsen flame; the vapours given off are condensed on the outside of a porcelain dish (or test tube) containing cold water, and held close above. A black, grey or brown metallic film is given by Sb, As, Bi, Pb, Cd, Zn, Sn, Hg. When this film is treated with dilute (20 per cent.) HNO_3, Sb and As are scarcely affected, Bi and Hg dissolve slowly, and the rest easily.

The test is now repeated with the difference that the thread is held at the top of the oxidising flame. Films of oxide are thus obtained with Sb, As, Zn (white), Bi, Sn (yellowish white), Pb (ochre yellow) and Cd (blackish brown).

The films of oxide may now be further examined in various ways. By breathing on the film to moisten it and then subjecting it to the fumes of HI, iodide films are obtained as follows:—Sb, As orange or yellow; Bi bluish-brown to pink; Sn yellowish-white; Pb yellow; Zn, Cd white. Hg does not give an oxide film, but the iodide may be obtained from the metallic film by first subjecting it to moist bromine vapour (which makes it first black and then colourless), and then to HI, which turns it scarlet.

The iodide films may now be subjected to the vapours of ammonium sulphide (best by blowing air through its solution by means of a wash-bottle with the long and short tubes reversed); the sulphide films so obtained are—Sb orange; As, Cd yellow; Bi brown; Hg, Pb black. Many further tests will suggest themselves; *e.g.* the metallic films of As and Sb may be distinguished by NaClO, and their oxide films by ammoniacal $AgNO_3$.

In all the above tests it is advisable to repeat the experiment with the *known* substance, and compare results.

* *In some cases, e.g. with tin compounds, it is better to use a mixture of* Na_2CO_3 *and KCN.* † *Especially if a little tin be added.*

‡ *Confirm by fusing with excess of* Na_2CO_3 *and a little* KNO_3. *Mn bluish green, Cr yellow.*

§ *Distinguished from oxygen by its greater solubility in water, by action of nitric oxide, or by alkaline pyrogallol.*

TO DISSOLVE A SUBSTANCE FOR ANALYSIS.

Boil the finely powdered substance with (1) water, (2) hydrochloric acid, (3) nitric acid (trying both dilute and strong acids), (4) aqua regia; removing the previous solvent in each case. If only a part dissolves, the solution may be examined separately.

If all these reagents fail to dissolve the substance*, fuse it (or that portion which is insoluble) with about five times its weight of dry sodium carbonate on platinum foil†. Extract the fused mass with a little boiling water and filter‡.

RESIDUE	SOLUTION
Wash first with strong Na_2CO_3 solution and then with water until no longer alkaline. Dissolve in dilute HNO_3 and test solution for metals§. If a portion remains insoluble the fusion should be repeated or special methods of attack should be adopted. (See page 53.)	Examine a portion for acids in the usual way, after acidification with HNO_3. Acidify the remainder with HCl and test for silica acid and for Al, Cr, Mn, Zn, As, Sn.

The solution for analysis is assumed to be neutral or slightly acid; if strongly acid it must be diluted or nearly neutralised with Na_2CO_3 before passing H_2S, or the excess of acid may be removed by evaporation. If the solution is alkaline it should be just acidified with dilute HNO_3, any precipitate produced being examined separately‖.

Cyanides, ferrocyanides, ferricyanides, &c., often greatly interfere with the ordinary process of examination for metals and, in the analysis of mixtures, it is advisable to destroy them by evaporation to dryness with strong sulphuric acid. This leaves the metals (including those contained in the complex anions) as sulphates.

Most insoluble ferrocyanides (or ferricyanides, &c.) may also be decomposed by boiling with caustic soda, sodium ferrocyanide going into solution, and the metal usually remaining as hydroxide. In the case of zinc ferrocyanide the latter will also dissolve as zincate, but may be separated as carbonate by passing CO_2.

If the given substance is a *metal* or an *alloy* it should be treated as follows: Heat the substance with rather strong nitric acid (*e.g.* about 1·3) until action ceases, evaporate to small bulk to remove excess of acid, add water and filter.

RESIDUE¶	SOLUTION
May contain Sb and Sn as hydrated oxides (possibly also Sb, Sn or Bi as arsenates or phosphates), (Au, Pt). Wash thoroughly and dissolve in concentrated sulphuric acid, boiling if necessary. Cool solution and cautiously add about twice its volume of concentrated HCl (boil if not clear) and dilute with an equal volume of water. Test portions of solution as follows:— 1. For Sb by the zinc and platinum foil test. 2. For Sn by treating with iron wire till colourless (to reduce to the stannous condition), and testing with $HgCl_2$. 3. For phosphate and arsenate by diluting, adding tartaric acid, making alkaline with NH_3, and testing with magnesia-mixture.	Examine for metals (except Sb, Sn) as usual.

* Amongst the commoner substances likely to remain insoluble after treatment with water and acids, the following may be mentioned:—

SiO_2, silicates. Sulphates of Ba, Sr (Ca). Fluoride of Ca. These are all decomposed or rendered soluble by the method of fusion with sodium carbonate.

Silver haloids (*e.g.* AgCl) are best treated with zinc and dilute H_2SO_4, metallic silver and zinc haloid being obtained. AgCl dissolves also in solutions of KCN or $Na_2S_2O_3$.

SnO_2 and *Sb_2O_5* may be fused with potassium cyanide and the resulting metals treated as usual.

Lead sulphate may be decomposed by boiling with strong soda solution; it is also soluble in strong solutions of ammonium acetate or tartrate.

Many *minerals* which cannot easily be attacked by any of the foregoing operations may be brought into a soluble state by fusion with $KHSO_4$ or with KHF_2. This treatment also serves for *ignited Fe_2O_3*, Al_2O_3, Cr_2O_3, which are very difficult to attack by acids.

Chrome iron ore is best attacked by fusion with sodium peroxide, a soluble chromate being formed and Fe_2O_3 left insoluble on extraction with water.

Carbon and *sulphur* are easily recognized by their behaviour on burning.

Calomel, although brought into solution by boiling with strong nitric acid or aqua regia, does not dissolve as such, but is converted into a mercur*ic* salt. Hence the state of the mercury must be verified in the original solid (*e.g.* by the blackening with NaOH).

† Platinum vessels are attacked by easily reducible metals such as Pb, Bi, Ag, also by caustic alkalis. If porcelain is used for the fusion, some Si and Al, &c., will be introduced. Hence in presence of reducible metals (indicated by the preliminary examination) special treatment is necessary. In the case of silicates for example, in presence of Pb, &c., the fluoride treatment is adopted (see note §). For fusion with caustic alkalis, silver or nickel crucibles may be used.

‡ The action of sodium carbonate in this operation is, generally speaking, to give an insoluble carbonate or oxide of the metal and a soluble sodium salt of the acid radicle, *e.g.*—

$$Na_2CO_3 + BaSO_4 \rightleftharpoons BaCO_3 + Na_2SO_4.$$

Such actions being generally limited and reversible, a large relative mass of sodium carbonate is used, and the process repeated if necessary.

§ When a substance has to be fused with sodium or potassium carbonates, it is necessary of course to examine for the alkalis in the original substance instead of in the product obtained by the fusion. In the case of silicates this may be done by heating the powdered substance with ammonium fluoride and strong H_2SO_4, by which treatment the silicon is eliminated as gaseous fluoride, the metals being left as soluble sulphates,

$$4NH_4F + SiO_2 + 2H_2SO_4 = 2(NH_4)_2SO_4 + 2H_2O + SiF_4.$$

Another method is to mix the finely powdered mineral (1 part) with *pure* $CaCO_3$ (about 8 parts) and NH_4Cl (about 1 part), and to strongly heat the mixture in a covered platinum crucible for about an hour. The mass is then extracted with water, and the solution (after removal of Ca by ammonium oxalate) is tested for the alkali metals.

‖ A precipitate here may be due to the separation of sparingly soluble acids (*e.g.* silicic, benzoic, salicylic, uric, boric) from their salts, to sulphur from polysulphides or thiosulphates, to certain metallic hydroxides or sulphides which behave acidic (*e.g.* $Sn(OH)_4$, $Pb(OH)_4$, As_2S_3, SnS_2) or to single insoluble cyanides from soluble 'double cyanides.'

¶ Or this residue may be fused with excess of caustic soda in a silver dish, extracted with a little water and alcohol added. Sodium stannate dissolves and pyroantimonate is pptd.

Another method is to mix the residue with KOH till alkaline, and then warm with sodium or potassium sulphide. This dissolves Sn and Sb as sulpho-salts, which can be examined by Table II A.

For explanation of the reactions which occur refer to General

EXAMINATION FOR ONE METAL.

If solid, dissolve in (1) water, (2) HCl, (3) HNO_3 (try both dilute and strong acids), (4) aqua regia. Otherwise fuse with Na_2CO_3.
If solution is alkaline, just acidify with HNO_3 (dilute), filter off any ppt., and examine it separately. [See p. 52.]
If solution is strongly acid, dilute, or nearly neutralize it, before Group 2.
Test portions of the solution as follows:

Group	Reagent	Metal	Treatment of ppt.		CONFIRMATORY TESTS in original solution or substance.
1.	Add dilute *Hydrochloric acid.*		Pour off liquid and shake ppt. with ammonia.		
	White ppt. indicates *	SILVER	Dissolved		(1) K_2CrO_4 crimson ppt. (2) The HCl ppt. turns violet on exposure to light.
		LEAD	Unchanged		(1) Dilute H_2SO_4 white ppt. (2) K_2CrO_4 yellow ppt. soluble in NaOH. (3) KI yellow ppt. soluble in boiling water.
		MERCURY Mercurous	Blackened		(1) Heat solid in bulb-tube with dry Na_2CO_3. Grey sublimate of metallic mercury. (2) NaOH black ppt. insoluble in NH_3. (3) Same as for Mercuric (1).
2.	Add dilute HCl and pass *Hydrosulphuric acid* gas. Heat.		Wash ppt. with water, and digest portions of it with hot *Ammonium sulphide* ‖	*Ammonium carbonate*	
	Ppt. indicates †	ARSENIC (yellow) ‡	Dissolved	Dissolved	(1) Try Marsh's test. Black stain on porcelain, soluble in NaClO. (2) Distinguish between As''' and As^{v} by adding $AgNO_3$ (in neutral solution $\begin{cases} \text{yellow} = As''' \\ \text{brick-red} = As^{v} \end{cases}$
		ANTIMONY (orange)	Dissolved	Undissolved	(1) Acidify dilute solution with HCl, pour it on to piece of zinc in contact with platinum foil; black stain on the platinum. (2) Marsh's test; black stain not dissolved by NaClO. [(3) Distinguish between Sb''' and Sb^{v} by $AgNO_3$ test.]
		TIN (*-ous* dark brown) (*-ic* dirty yellow)	Dissolved	Undissolved	(1) Add small piece of zinc + dilute HCl. Allow to stand. Pour off liquid, and dissolve residue in strong hot HCl. Add $HgCl_2$. White ppt. (often turning grey on heating). (2) Distinguish between Sn'' and Sn^{iv} by adding $HgCl_2$ to original solution. White ppt. Sn''. No ppt. Sn^{iv}.
		MERCURY Mercuric (black)	Undissolved		(1) Acidulate with HCl and add metallic copper. [Nitric acid must be absent.] Bright deposit of metallic mercury on the copper. Wash, dry, and heat in dry test-tube. Grey sublimate of Hg. (2) NaOH yellow ppt. (3) Dry test same as Mercurous (1).
		LEAD (black) §	Ditto		See Group 1.
		COPPER (brownish-black)	Ditto (nearly)		(1) NH_3 pale blue ppt. redissolving at once in excess to deep blue solution. (2) K_4FeCy_6 chocolate ppt.
		BISMUTH (brownish-black)	Ditto		(1) NH_3 white ppt.; dissolve it in least possible HCl, and add much water; white milky ppt. (2) $SnCl_2$ + NaOH black ppt. (3) K_2CrO_4 yellow ppt. insoluble in NaOH.
		CADMIUM (yellow)	Ditto		(1) KCN in excess + H_2S yellow ppt. (2) NH_3 white ppt. easily soluble in excess.
	Add a few drops of nitric acid and boil. Then add NH_4Cl in excess, and *Ammonia*. Boil.		Test a *nitric* acid solution of original substance (or of the NH_3 ppt.) with *ammonium molybdate* in excess. Yellow ppt. on heating shews a PHOSPHATE. Test original solution with *Caustic soda.*		
		ALUMINIUM ¶ (white)	White gelatinous ppt.; *soluble* in excess; repptd. by NH_4Cl		Heated on charcoal usually gives white infusible mass. Treated with $Co(NO_3)_2$ and again heated, blue mass.

Unless the contrary is stated, each reagent must

be added until *no further effect* is produced.

3.	Ppt. indicates	CHROMIUM ¶ (bluish-green)	Green ppt.; soluble in excess; repptd. by boiling	(1) Fuse with $Na_2CO_3 + KNO_3$ on platinum foil**. Yellow mass. Dissolve in water, add acetic acid and lead acetate. Yellow ppt. (2) Distinguish between Cr''' and Cr^{vi} by lead acetate test in original solution. [See acids.]
		IRON ¶ (reddish-brown)	Reddish-brown ppt. *Ferric* } insoluble in excess; Dirty green ppt. *Ferrous* } insoluble in excess	(1) K_4FeCy_6 {pale blue ppt. Ferrous; dark blue ppt. Ferric. (2) KCyS {no colour. Ferrous; blood red colour. Ferric. (3) $K_6Fe_2Cy_{12}$. Dark blue ppt. Ferrous. No ppt. Ferric††.
		PHOSPHATE of Ba, Sr, Ca, or Mg (white)	White ppt. insoluble in excess	Dissolve original substance (or NH_3 ppt.) in least possible quantity of HCl. Add some acetic acid and large excess of sodium acetate. [A ppt. here indicates Oxalate or Fluoride of Ca(BaSr), or phosphate of Fe(CrAl).] Add a few drops of $FeCl_3$; yellowish-white ppt. confirms Phosphate of Ca Ba Sr Mg. In this case add $FeCl_3$ until solution is red. Boil. If not colourless add a drop of NH_3. Filter. Test filtrate for Ca Ba Sr Mg by **5** and **6**.
		OXALATE of Ca(BaSr) (white)	White ppt. insoluble in excess	Heat original substance (or NH_3 ppt.) to low redness. Add acetic acid. Effervescence indicates Oxalate. Filter if necessary. Test solution for Ca (Ba, Sr) by **5**.
		FLUORIDE [or BORATE, &c.] of Ca(BaSr) (white)	White ppt. insoluble in excess	Test for Fluoride by heating with strong H_2SO_4. See Acids. Fuse original substance with Na_2CO_3. Extract fused mass with water. Filter. Test residue for Ca, &c., and solution for Fluoride, Borate, &c.
		SILICA (white)		Acidify with HCl. Evaporate to dryness. Digest residue with HCl. Residue insoluble in HCl = Silica.
4.	Add NH_4Cl, NH_3 and *Ammonium sulphide.*		Test original solution with *caustic soda.*	
	Ppt. indicates	NICKEL (black)	Pale green ppt. insoluble in excess	(1) Borax bead brownish-violet in oxidising flame. (2) Add KCN until ppt. formed is just redissolved. Boil for some time in open dish. Add NaClO and allow to stand. Black ppt.
		COBALT (black)	Blue ppt. insoluble in excess	(1) Borax bead blue in both flames. (2) Add KCN, &c., as for Nickel; NaClO no ppt.
		MANGANESE (buff or pink)	White ppt. insoluble in excess. Rapidly turning brown when shaken with air	(1) Fuse with $Na_2CO_3(+KNO_3)$ on platinum foil. Bluish-green mass. (2) Distinguish between Mn'' and Mn''', Mn^{iv}, Mn^{vi}, &c., by boiling with HCl {Cl evolved—Mn''', Mn^{iv}, Mn^{vi}, &c.; no effect—Mn''.
		ZINC (white or greenish)	White ppt. *soluble* in excess	(1) Pass H_2S into the NaOH solution. White ppt. (2) Heat on charcoal. Usually, yellow mass when hot, white when cold. Add $Co(NO_3)_2$ and again heat. Green mass.
5.	Add NH_4Cl in excess, NH_3 and *Ammonium carbonate.*		Test original solution with Calcium Sulphate	
	White ppt. indicates	BARIUM	Immediate white ppt.	(1) K_2CrO_4 yellow ppt. (2) H_2SiF_6 translucent crystalline ppt. (3) Flame test, green.
		STRONTIUM	White ppt. on standing or heating	(1) Flame test, crimson. (2) H_2SiF_6, and K_2CrO_4 in dilute solution, no ppts.
		CALCIUM	No ppt.	(1) (In absence of Ba and Sr) Ammonium oxalate + NH_3 white ppt. Soluble in HCl; insoluble in acetic acid. (2) Flame test, orange red.
6.	Add NH_4Cl, NH_3 and *Sodium phosphate.* Stir. White ppt. MAGNESIUM.			(Crystalline from dilute solutions, or on standing.)
7.	Test portions of original solution for		AMMONIUM	(1) Boil with NaOH. Odour of NH_3 produced. (2) H_2PtCl_6 yellow ppt. (in lines on stirring). (See Potassium.)
			POTASSIUM	(1) (In absence of NH_4.) Acidify strong solution with HCl. Add $PtCl_4$. Stir. Yellow ppt. in lines‡‡. (2) Flame test, violet.
			SODIUM	(1) Flame test, intense yellow. Fixed residue on heating.

* A white ppt. which dissolves at once in cold water probably indicates a *Barium* salt. One which readily dissolves in slight excess of HCl probably *Antimony* [or *Bismuth*.

† { A white or nearly white ppt. which does not settle is probably Sulphur, indicating an *oxidising agent*.
If a ppt. of Sulphur is obtained, with much change of colour, filter off the ppt., boil filtrate to expel H_2S, and proceed with this, instead of original solution.
An orange solution changing to green with pptn. of sulphur indicates Chromium as Cr''.

‡ If arsenic is found in a solution it is probably present in the *acid* radicle and another metal should therefore be looked for.

Table, p. 72, and to special reactions of each metal.

PRELIMINARY EXAMINATION FOR ACID RADICLES.

1. Treat the solid substance (or strong solution) with *dilute Hydrochloric acid* in the cold. Afterwards heat.		CONFIRMATORY TESTS.
Effervescence *in the cold* with evolution CO_2 (detected by pouring the evolved gas into lime-water and shaking)	CARBONATE or Cyanate*	Further confirmation not usually required. If soluble, $BaCl_2$ or $CaCl_2$ gives white ppt. soluble in acids with effervescence. (N.B. Cyanides usually contain carbonates.)
" " " with evolution of chlorine (detected by odour, colour, and action on wet litmus paper) .	HYPOCHLORITE †	(1) $MnCl_2$, brown ppt. (2) Solution bleaches litmus, writing-ink, &c. (N.B. Hypochlorites always contain chlorides.)
Evolution of H_2S (detected by odour and action on lead acetate paper)	SULPHIDE ‡	If soluble in water, (1) Sodium nitroprusside, violet coloration. (2) Silver coin stained black.
" " SO_2 (detected by odour, and by action on $K_2Cr_2O_7$ §)	SULPHITE	(1) Zn + dil. HCl. H_2S evolved. Detected as above. (2) $AgNO_3$, white ppt. Blackens on heating. (N.B. Sulphites usually contain sulphates.)
" " SO_2 with deposition of sulphur	THIOSULPHATE	Same as for Sulphite. Distinguished by deposition of yellow sulphur on adding HCl and heating.
" " oxides of nitrogen	Nitrite	(See below.)
" " HCN (detected by odour, or by absorbing evolved gas on filter paper spotted with NaHO, and applying confirmatory test to the spot) . . . . . . Repeat test for sulphide, using *strong* HCl, since some sulphides are not decomposed by the dilute acid .	CYANIDE	(1)‖ To neutral or alkaline solution, add $FeSO_4$, $FeCl_3$, and HCl; dark blue ppt. or coloration. (Prussian blue.) (2) $AgNO_3$, white ppt. soluble in NH_3, insoluble in dil. HNO_3. (N.B. Cyanides often contain cyanates and carbonates.)
2. Heat solid substance¶ with concentrated *Sulphuric Acid*.		
The above salts give much the same result as with hydrochloric acid. In addition to which	•	
Evolution of ClO_2 (yellow explosive gas) and liquid turning yellow	CHLORATE	(1) Indigo bleached in the *cold*, on the addition of *sulphurous acid*. (2) Heated, they evolve O, becoming chlorides.

For explanation of the changes which occur, see next page

and also special reactions of the respective Acid Radicles.

,, ,,	Oxides of nitrogen (yellow or brown, with characteristic odour)	NITRATE	(1) Add $FeSO_4$ in excess to *cold* solution; gradually pour in strong H_2SO_4. Brown or pink ring where liquids meet. (2) Brucine in presence of strong H_2SO_4. Red colour.
		or Nitrite	(1) KI + dilute HCl. Iodine liberated. Detected by starch. (2) $FeSO_4$ brown colour, with or without H_2SO_4.
,, ,,	Acetic acid vapour (recognized by odour)	ACETATE	(1) $FeCl_3$, red colour, bleached by HCl, not by $HgCl_2$. This test must be applied in *neutral* solution. (2) Heated with strong H_2SO_4 and a drop of alcohol, odour of ethyl acetate.
,, ,,	CO (burns with blue flame) and CO_2 (detected by lime-water as above) without blackening	OXALATE (Ferricyanide)	Proceed to Table on page 60.
,, ,,	CO alone, *without blackening*	FERROCYANIDE Cyanide Formate	
,, ,,	CO *with blackening* of the liquid . . .	TARTRATE (blackens at once) or CITRATE (blackens slowly)	
,, ,,	I (violet fumes, which colour starch paste blue)	IODIDE	
,, ,,	Br (brownish-red vapours, condensing to deep red liquid)	BROMIDE Bromate or Hypobromite	
,, ,,	SiF_4 (white clouds which deposit white gelatinous silica on a wet rod) . . .	FLUORIDE or SILICOFLUORIDE	
,, ,,	HCl (colourless pungent fumes, forming white clouds in the air)	CHLORIDE	

If none of these results with the above reagents, the salt may be a phosphate, arsenate, borate, chromate, sulphate, silicate. Proceed to Table on page 60.

* Cyanates treated with dilute acids evolve CO_2, and form an ammonium salt. The latter may be confirmed by adding caustic potash till alkaline, and Nessler's solution, when a yellow or brown colouration is obtained.

† Chlorates may also evolve chlorine mixed with ClO_2.

‡ Sulphocyanates give H_2S and CO_2. Distinguished by wet tests.

§ Strong HCl vapours will also turn pot. bichromate green after a time, and the odour of HCl is sometimes mistaken for that of SO_2; confirmatory test is therefore absolutely necessary.

‖ Mercuric cyanide must be decomposed by H_2S before applying confirmatory test for cyanide.

¶ If the substance given is a liquid, it should be evaporated *just* to dryness; (if the solution is acid it must be just neutralized before evaporation in order to fix volatile acids). In many cases a strong solution may be used with excess of sulphuric acid; but the effects are not so well marked.

EXPLANATION OF PRELIMINARY ACID TABLE.

The following equations may be taken as typical of the reactions which occur:

Carbonate ...... $Na_2CO_3 + 2HCl = 2NaCl + H_2O + \mathbf{CO_2}$.

Hypochlorite ... $\begin{cases} NaClO + HCl = NaCl + HClO \\ HClO + HCl = H_2O + \mathbf{Cl_2} \end{cases}$.

Sulphide .... $Na_2S + 2HCl = 2NaCl + \mathbf{H_2S}$.

Sulphite .... $Na_2SO_3 + 2HCl = 2NaCl + H_2O + \mathbf{SO_2}$.

Thiosulphate ... $Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + \mathbf{SO_2} + \mathbf{S}$.

Cyanide .... $KCN + HCl = KCl + HCN$.

Cyanate .... $\begin{cases} KCNO + HCl = HCNO + KCl \\ HCNO + H_2O + HCl = \mathbf{NH_4Cl} + \mathbf{CO_2} \end{cases}$.

Chlorate .... $3KClO_3 + 2H_2SO_4 = 2KHSO_4 + KClO_4 + H_2O + \mathbf{2ClO_2}$.

Nitrate .... $\begin{cases} KNO_3 + H_2SO_4 = KHSO_4 + HNO_3 \\ 4HNO_3 \text{ (in part)} = 2H_2O + \mathbf{4NO_2} + O_2 \end{cases}$.

Nitrite............ $2KNO_2 + 2H_2SO_4 = 2KHSO_4 + NO + NO_2 + H_2O$.

Acetate .... $CH_3COOK + H_2SO_4 = KHSO_4 + \mathbf{CH_3COOH}$.

Oxalate .... $\begin{cases} COOH \\ COOH \end{cases} - H_2O = \mathbf{CO} + \mathbf{CO_2}$.

Ferrocyanide ... $K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + \mathbf{6CO}$.

Formate .... $HCOOH - H_2O = \mathbf{CO}$.

Cyanide .... $2KCN + 4H_2SO_4 + 2H_2O = 2KHSO_4 + 2(NH_4)HSO_4 + \mathbf{2CO}$ (in part).

Iodide .... $\begin{cases} KI + H_2SO_4 = KHSO_4 + HI \\ 2HI + H_2SO_4 = 2H_2O + SO_2 + \mathbf{I_2} \text{ (in part)*} \end{cases}$.

Bromide .... Same reaction as iodide, but much HBr escapes undecomposed.

Bromate .... $\begin{cases} KBrO_3 + H_2SO_4 = KHSO_4 + HBrO_3 \\ 4HBrO_3 - 2H_2O = \mathbf{2Br_2} + 5O_2 \text{ (in part)} \end{cases}$.

Hypobromite ... Same reaction as for hypochlorite.

Fluoride .... $\begin{cases} CaF_2 + H_2SO_4 = CaSO_4 + 2HF \\ 4HF + SiO_2 = 2H_2O + \mathbf{SiF_4} \end{cases}$

Silicofluoride ... $K_2SiF_6 + H_2SO_4 = K_2SO_4 + \mathbf{SiF_4} + 2HF$.

Chloride .... $NaCl + H_2SO_4 = NaHSO_4 + \mathbf{HCl}$.

Tartrate ....
Citrate............ } Reactions not definite.

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* If the HI were much in excess of the H_2SO_4, some H_2S might be evolved—

$$8HI + H_2SO_4 = H_2S + 4H_2O + 4I_2.$$

EXAMINATION FOR ACID RADICLES IN THE WET WAY.

Preparation of Solution.

The substance, if solid, must be dissolved if possible in water, since acids are obviously inadmissible (except in the places mentioned, *e.g.* Groups 2 and 3).

If *insoluble in water*, the most *general* method is to boil with a strong solution of sodium carbonate for some time (or, in case of acids not decomposable by heat, to fuse with solid sodium carbonate and boil residue with water) and filter. In this way the acid is usually obtained as a soluble sodium salt, while the base remains as an insoluble carbonate or oxide, *e.g.*

$$CaF_2 + Na_2CO_3 = \underbrace{CaCO_3}_{\text{residue}} + \underbrace{2NaF.}_{\text{solution}}$$

If metals are present in solution which would interfere with the tests about to be applied (as a rule, all except K, Na or (NH_4)), they must be removed before proceeding. [The necessity, or otherwise, of removing metals, is roughly indicated by boiling a portion of the solution with Na_2CO_3; if no ppt. is produced, it is *usually* safe to proceed. The previous examination for metals, however, is a better guide.] This may in most cases be done by boiling or fusing with Na_2CO_3 as above. [Phosphates of Al, Ca, Ba, &c. are very imperfectly decomposed in this way, but they will have been identified during the examination for metals.]

The solution, after boiling or fusing with Na_2CO_3, must be just acidified with dilute HNO_3 to remove the excess of Na_2CO_3, and gently heated to expel CO_2.

Hydrosulphuric acid may be used to remove metals of groups 1 and 2, the filtrate being afterwards heated to expel excess of H_2S. This method of removing the metal is necessary in such cases as mercuric cyanide and tartar-emetic; but here great care is necessary since HCN would be lost in removing the H_2S by evaporation, or if oxidising agents are present organic acids might be destroyed during this process. Hence in these cases the H_2S should be added as nearly as possible in the exact quantity necessary to precipitate all the metal.

Dilute sulphuric acid and alcohol is sometimes employed in case of Pb, Ba, Sr and Ca.

EXAMINATION FOR ONE ACID RADICLE.

The presence of Carbonate, Hypochlorite, Sulphide, Sulphite and Thiosulphate must be ascertained from the Preliminary Examination, and special tests mentioned on page 56. Arsenate, Arsenite, Chromate, Manganate, Permanganate (also Phosphate, Oxalate, when present as Ca, &c. salts) will have been detected during the Examination for Metals.

Dissolve the substance if possible in water. Test a portion of the solution with sodium carbonate; if this gives a ppt. the solution must be boiled for some time with excess of Na_2CO_3 (to remove metals), filtered, the filtrate made just acid with dilute HNO_3*†, and warmed to expel CO_2. [Test evolved gas for HCN by special test; see page 38.]

If the substance is insoluble in water it must be boiled† with Na_2CO_3, and treated as above.

If the original solution is alkaline, it must be just acidified with dilute HNO_3†.

Test portions of the solution as follows:—

1. Carefully neutralize with NH_3 (if not already neutral) and add *Silver Nitrate* in slight excess. If *no ppt.* is produced, it is only necessary to look for Nitrate, Chlorate, Fluoride, Silico-fluoride, Sulphate, Acetate, Borate (Nitrite).
A ppt. may indicate Phosphate, [Arsenite] Iodide (yellow). [Arsenate, brick-red.] [Chromate, crimson.] [Sulphide, black.] Ferricyanide (orange). Oxalate, Tartrate, Citrate, Chloride, Cyanide, Ferrocyanide, Sulpho-cyanate (white). [Carbonate], Bromide (white or yellowish-white). [Sulphite, white turning grey on heating.] [Thiosulphate, white quickly turning brown or black.] If the solution is not too dilute, Borate, Acetate, Sulphate, Nitrite (white).

2. Add excess of dilute HNO_3 and *Silver Nitrate*‡.

Ppt. indicates (For colours see I.)	Digest ppt. with ammonia	CONFIRMATORY TESTS [These may often be applied to the original substance; it is safer however to employ the solution from which metals (other than K, Na, NH_4) have been separated as above, this solution being evaporated just to dryness if the solid is required.]
CHLORIDE	Easily soluble	(1) Heat solid (or strong solution) with MnO_2 and concentrated H_2SO_4; chlorine evolved, recognized by action on litmus odour, &c. (2) Heat solid with dry $K_2Cr_2O_7$ and concentrated H_2SO_4; CrO_2Cl_2 (red gas) evolved, which when passed into water gives chromic acid (detected as on page 13) and HCl.
CYANIDE	,,	Prussian blue test. See Preliminary Table.
SULPHOCYANATE	,,	$FeCl_3$, blood red colour bleached by $HgCl_2$, but not by dilute HCl.
FERRICYANIDE	,,	(1) $FeSO_4$, dark blue ppt. (2) KI and dilute HCl; iodine liberated on heating. (3) $FeCl_3$, no ppt. (if pure).
BROMIDE	Sparingly soluble	(1) Add a few drops of chlorine water and shake up with CS_2; the latter is coloured yellow or orange. (2) Heat with strong H_2SO_4 and MnO_2; Bromine is evolved (orange-red fumes).
IODIDE	(Nearly) insoluble	(1) Add a few drops of chlorine water and shake up with CS_2; the latter is coloured violet. (2) Strong H_2SO_4 evolves violet fumes of iodine on heating.
FERROCYANIDE	Insoluble	(1) $FeCl_3$, dark blue ppt. (2) $CuSO_4$, chocolate ppt. (3) $FeSO_4$, pale blue ppt.

Chromate may be pptd. here from strong solutions if insufficient HNO_3 is present. Sulphide also if not previously destroyed during acidification.

3. Add dilute HCl and *Barium Chloride*. White ppt. indicates

White ppt. indicates	
SULPHATE	$Sr(NO_3)_2$, white ppt. (slowly in dilute solutions).
SILICOFLUORIDE	Heated alone or with strong H_2SO_4 in platinum vessel, SiF_4 evolved, recognized by wet rod.

4. Add NH_3 till just alkaline (filter if necessary†) and *Calcium Chloride*

White ppt. indicates¶	Digest ppt. with acetic acid	
OXALATE	Undissolved	Treated with strong H_2SO_4 and MnO_2, CO_2 evolved without heating.
FLUORIDE	§,,	(1) Heated in a platinum vessel with strong H_2SO_4, HF is evolved, recognized by etching test. (2) Heated in a test-tube with strong H_2SO_4, SiF_4 is evolved, recognized by wet rod.
PHOSPHATE	Dissolved	(1) In neutral solution $AgNO_3$, yellow ppt. (2) In NH_3 solution, Magnesia mixture, white ppt. (3) In HNO_3 solution $(NH_4)_2MoO_4$, yellow ppt. on heating. (4) In acetic acid solution $FeCl_3$, yellowish ppt.
[ARSENATE]	,,	(1) $AgNO_3$ in neutral solution, brick-red ppt. (2) Excess of H_2S in presence of HCl, yellow ppt. on boiling. $(NH_4)_2MoO_4$, Magnesia mixture and $FeCl_3$, the same as with Phosphate.
BORATE	§,,	(1) Mixed with concentrated H_2SO_4 and alcohol, the latter when ignited burns with a green edged flame. (2) Turmeric paper dipped into solution acidified with HCl, and then dried at gentle heat, is turned orange; KOH turns this greenish or black.
TARTRATE	§,,	(1) Potassium acetate + acetic acid, white crystalline ppt. on shaking (in strong solution). (2) Mirror test with ammoniacal silver nitrate. (3) $FeSO_4$, H_2O_2 and NaOH test. (4) Mixed with NaOH in excess and a few drops of $KMnO_4$; green colour changing to brown ppt. on heating.
CITRATE‖	,,	(1) Lime water added to *neutral* solution, no immediate ppt.; ppt. on boiling for some time. (2) Ammoniacal silver nitrate negative. (3) $FeSO_4$, H_2O_2 and NaOH, negative. (4) NaOH and $KMnO_4$; green colour not changed on heating. (5) Potassium acetate; negative.
SILICATE	Decomposed, often with separation of silicic acid	Solution evaporated to dryness with HCl and heated leaves residue insoluble in HCl.

5. Add *Ferric Chloride* to *neutral* solution

Blood-red colour indicates	Sulphocyanate. The red colour is bleached by $HgCl_2$; not by dilute HCl. Acetate. Formate. The red colour is destroyed by dilute HCl. Iodide. The red solution shaken with CS_2; the latter is coloured violet.	
Yellowish white ppt. indicates	Phosphate, Arsenate	See tests above.
[Dark blue ppt. indicates	Ferrocyanide]	See tests above.

If no definite results are obtained with any of the above tests, examine specially for NITRATE (by H_2SO_4 and $FeSO_4$ test), CHLORATE (by indigo and SO_2 test, &c.). Also for Borate and Cyanide (by tests mentioned above), since these may have been overlooked. It is advisable also to test for CHROMATE, MANGANATE and PERMANGANATE [pages 13—18], in case these should have been missed in the examination for metals.

If no acid radicle is found, the substance may be an oxide or hydroxide of the metal. [See page 62.]

* In some cases (*e.g.* silicates) mere boiling is insufficient, and the substance must be fused with Na_2CO_3. This method of removing metals by Na_2CO_3 is not universally applicable; in the cases of mercuric cyanide and tartar-emetic, for example, the metal should be removed by cautious treatment with H_2S.

† Care must be taken to add only just the quantities of acid or of ammonia necessary, since the presence of much ammonium salt may prevent the precipitation of calcium tartrate fluoride, &c. A precipitate on acidification may be silicic or some other sparingly soluble acid; also certain metallic hydroxides or sulphides which behave acidic, *e.g.* $Sn(OH)_4$, $Al(OH)_3$, As_2S_3, SnS_2, or insoluble cyanides, &c. A precipitate on adding ammonia to the acid solution may also indicate silicic acid or else imperfect separation of the metals.

‡ In most cases it is sufficient to digest the previous precipitate (from I.) with dilute HNO_3, but it is preferable to make a fresh test as here indicated.

§ Calcium tartrate becomes crystalline after a time, and is then nearly insoluble in acetic acid. The precipitation of calcium tartrate, borate or fluoride may be prevented if too much ammonium salt is present.

‖ Calcium citrate may not be precipitated until the solution is boiled.

¶ *Sulphate* and *Ferrocyanide* may also be pptd. here from strong solutions.

CONCLUDING REMARKS ON THE EXAMINATION OF SINGLE INORGANIC SUBSTANCES (SOLID OR LIQUID).

If no metal is present, the given substance may be a free acid or acidic oxide, or a non-metallic element or compound; if no acid is found, it may be a metal (or alloy) or a metallic oxide or hydroxide. If neither metal or acid can be detected, the given substance may be pure water or hydrogen dioxide.

The common non-metallic elements will be easily recognized by their properties and by their products of oxidation; *e.g.* carbon, sulphur, phosphorus, boron and silicon (amorphous) burn to CO_2, SO_2, P_2O_5, B_2O_3 and SiO_2, which are all easily identified by the tests mentioned above. Or they may be oxidised with strong HNO_3, in which case sulphur will give H_2SO_4, phosphorus H_3PO_4, iodine HIO_3, and so on. Compounds of non-metallic elements such as PCl_5 or ICl will be recognized by the acids resulting from their decomposition by water.

Metallic carbides, silicides, nitrides or phosphides yield characteristic hydrides of the non-metallic element when acted upon by water (or in some cases by acids or alkalis). *E.g.* calcium carbide gives acetylene, aluminium carbide gives methane, and calcium nitride gives ammonia. Silicon carbide when fused with alkalis gives a silicate and carbonate.

When it is concluded that the substance must be a metallic oxide or hydroxide it is generally advisable to make experiments with a view of ascertaining the class to which it belongs. It must be remembered however that the classification of oxides as basic, acidic, peroxide or compound oxide is often merely relative and is only intended to indicate broadly the more pronounced behaviour of the substance. ZnO and Al_2O_3 for example are basic as regards their behaviour with acids, but acidic as regards caustic soda; PbO_2 and MnO_2 are often classed as peroxides, but may also be looked upon as basic oxides corresponding to the unstable Pb^{iv} and Mn^{iv} salts.

The following suggestions will serve to indicate the kind of experiments which may be carried out in making this rough classification:—

Heat the oxide with concentrated HCl	Chlorine evolved	Peroxide, or acidic oxide of metal.
Shake up with a strong solution of Na_2CO_3 and warm if necessary	CO_2 evolved*	Acidic oxide (of either metal or non-metal).
Make into a paste with water and pour into an excess of dilute HCl, *keeping the mixture cold*	H_2O_2 liberated†	Peroxide of Ba, Sr, Ca, Na, K (Zn, Cd, Cu).

If none of these effects are observed the oxide is probably basic; in this case dissolve in HCl or dilute H_2SO_4 and ascertain whether the result is an *-ous* or *-ic* salt.

When soluble, basic oxides and peroxides give an alkaline reaction if shaken with water and litmus, and acidic oxides similarly give an acid reaction. (In applying this test see that the effect is not merely due to impurity in the specimen of oxide given.)

Compound oxides usually behave as mixtures; Fe_3O_4 for example, when treated with acids, yield salts corresponding to the two basic oxides FeO and Fe_2O_3 and Pb_3O_4, when acted upon by HNO_3, gives the nitrate corresponding to PbO together with a residue of PbO_2.

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* SiO_2 requires fusion with Na_2CO_3.

† Hydrogen dioxide is easily detected by (1) shaking up the solution with a mixture of $K_2Cr_2O_7$, dilute H_2SO_4 and ether; blue compound, soluble in ether. (2) Titanium dioxide dissolved in H_2SO_4 gives orange-red colour (or yellow if only traces of H_2O_2 are present). (3) Ag_2O, $KMnO_4$, PbO_2, &c. are reduced. Iodine is liberated from HI.

SUGGESTIONS FOR THE RECOGNITION OF SOME OF THE COMMON GASES.

	Approximate specific gravity air=1	With water at ordinary temperatures	With strong solution of caustic soda	Distinguishing properties or reactions
Oxygen	1·1	Nearly insoluble	—	Rekindles glowing splinter. Absorbed by pyrogallol + KOH, giving a brown solution. With NO gives brown fumes.
Hydrogen	0·07	— —	—	Burns with non-luminous flame producing water.
Nitrogen	0·97	— —	—	Negative to all the tests here mentioned.
Carbon monoxide	0·97	— —	—	Burns with blue flame. Absorbed by CuCl in ammonia or in HCl solution. Liberates I from I_2O_5 on warming. $PdCl_2$ black stain.
Nitric oxide	1·04	— —	—	Gives reddish fumes with air or oxygen. $FeSO_4$ gives brown colour.
Methane	0·56	— —	—	Burns with fairly luminous flame.
Ethylene	0·97	— —	—	Burns with brightly luminous flame. Absorbed by fuming sulphuric acid or by bromine water.
Acetylene	0·90	About 1 in 1 by vol.	—	Burns with very luminous smoky flame. Gives red ppt. with CuCl in ammonia solution. Liberates I from I_2O_5 on warming.
Nitrous oxide	1·53	— 1 in 1 —	—	Rekindles glowing splinter. Gives no red fumes with NO.
Carbon dioxide	1·53	— 1 in 1 —	Easily absorbed, giving carbonate	Lime water, white ppt. soluble in excess of CO_2.
Chlorine	2·45	— 2 in 1 —	— hypochlorite and chloride	Yellowish green. Bleaches moist litmus. Liberates I from KI, and Br from KBr.
Cyanogen	1·80	— 4·5 in 1 —	— cyanide & cyanate	Burns with pink flame. Test KOH solution for cyanide, &c.
Hydrogen sulphide	1·19	— 3 in 1 —	— sulphide	Burns with bluish flame. Lead acetate paper blackened.
Sulphur dioxide	2·22	— 40 in 1 —	— sulphite	Odour. Bleaches potassium permanganate. Turns potassium bichromate green.
Hydrogen chloride	1·27	— 450 in 1 —	— chloride	Dense white fumes with NH_3. Test solution for chloride.
Hydrogen bromide	2·79	— 600 in 1 —	— bromide	Same as chloride.
Hydrogen iodide	4·4	— 420 in 1 —	— iodide	Same as chloride.
Ammonia	0·59	— 800 in 1 —	Easily dissolves	Dense white fumes with HCl. Red litmus turned blue. Odour.
'Peroxide' of nitrogen (B.P. 22°)	2·6 at 26·7 Variable with t. and P.	Decomposes, forming HNO_3 and nitric oxide	Easily absorbed, giving nitrite and nitrate	Reddish brown, darker at higher temperatures. $FeSO_4$, brown colour. Test NaOH solution for nitrate and nitrite.

Bromine **fumes (orange-red) are easily recognised; they dissolve in NaOH solution, giving colourless solution of bromide, hypobromite, &c.** ***Silicon tetrafluoride*** **is recognised by its action on water, giving gelatinous silicic acid and hydroflurosilicic acid.** ***Chlorine dioxide*** **is yellow, explosive on heating, and dissolves in alkalis to give chlorate and chlorite.**

EXAMINATION FOR MORE THAN ONE METAL.

EXPLANATION OF THE GENERAL SCHEME.

When a substance is brought into contact with water the following changes may occur:—(*a*) The substance may in the first instance combine with the solvent to form a *hydrate* [*e.g.* $CuSO_4$ gives $CuSO_4 . 5H_2O$, &c.]. (*b*) It may dissolve '*unchanged*' [*e.g.* cane sugar, urea]. (*c*) Complete or partial *hydrolysis* may take place in the sense salt + water $\rightleftarrows$ acid + base (*e.g.* $MX + HOH \rightleftarrows MOH + HX$). Arsenic trichloride, for example, gives arsenious and hydrochloric acids, and many normal salts give basic salt + free acid. (*d*) In addition to these effects acids, salts and bases may, according to theory, undergo electrolytic dissociation on *ionisation* in the sense $MX \rightleftarrows M^{\cdot} + X'$; $M_2X \rightleftarrows 2M^{\cdot} + X''$ *, and so on. The extent to which this change takes place depends principally on the nature of the compound and solvent, and on the dilution. Most salts when dissolved in water become highly ionised even at moderate dilution (mercuric cyanide and some other mercuric and cadmium salts being exceptional), whereas the behaviour of acids and bases is very variable; the stronger the acid or base the greater is the ionisation at a given dilution. The degree of ionisation becomes greater as the dilution increases, so that at infinite dilution all acids (or bases) would be equally strong.

If the proportion of solvent is limited, *i.e.* if excess of solid is present, the latter will continue to dissolve until, at a given temperature, there is equilibrium between the solution and solid; the solution is then normally saturated with respect to this particular solid. In the case of substances with dissolve unchanged, the concentration corresponding to this saturation value can be directly measured by ordinary solubility determinations. But if the compound undergoes partial ionisation, the case is not so simple; equilibrium is then established on the one hand between the solid and the non-ionised part of it in solution, the concentration of this non-ionised part having then a definite value = S. But further there is, as above indicated, equilibrium between the ionised and non-ionised part of the compound in solution. If for simplicity we consider the case of a binary electrolyte MX dissociating into two univalent ions $M^{\cdot} + X'$, and denote by a, b and c the concentrations (expressed in formula weights per unit volume) of M, X and MX respectively, it follows from the law of mass action that $\frac{a \times b}{c} = k$ (where k is a constant depending on the nature of the substance and on the temperature).

In the case of a saturated solution $c = S$, and the value of $a \times b$ is then called the solubility-product. If this value is exceeded, precipitation will take place, or the solution may remain supersaturated, whereas if the value is not attained more solid will dissolve.

From the above relation it follows that the concentration of MX may be increased not only by addition of more of the compound itself, but also by addition of one of the ions, since if a is increased, c must increase also with diminution (or 'suppression') of b.

* The latter in stages; *e.g.* $M_2X = M^{\cdot} + MX'$ and further, $MX' = M^{\cdot} + X''$.

Hence precipitation from a previously unsaturated solution can often be brought about by addition of a sufficiently strong solution of a salt (or strong acid or base) which contains an ion in common. Examples of this are found in the precipitation of solutions of sodium or barium chlorides by hydrochloric acid and in the 'salting out' of soaps by sodium chloride. Upon the same principle may be explained the advisability of adding excess of the precipitating reagent in analysis, and the common practice of washing precipitates which are somewhat soluble with a salt solution (*i.e.* one containing an ion in common) instead of with pure water.

When a substance which is 'insoluble' in water dissolves in an acid or in a solution of some salt, changes take place which for the most part can easily be interpreted in terms of the ionisation hypothesis. Metals dissolving in acids, for example, are changed from the 'neutral' to the ionic, or electrically charged, condition [*e.g.* $Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2$]. Salts of weak acids, such as calcium oxalate, dissolve in strong acids owing to the tendency to form the less ionised weak acid; the concentration of the anions of the weak acid is in this way lowered, and the hitherto saturated aqueous solution of the nearly insoluble salt becomes now unsaturated, since the solubility product is no longer reached, and more solid dissolves (see above). The states of equilibrium may briefly be represented as follows:—

$$(1)\ \underset{\text{solid}}{MX} \rightleftharpoons \underset{\substack{\text{saturated}\\\text{solution}}}{MX}. \quad (2)\ MX \rightleftharpoons M^{\cdot\cdot} + X''. \quad (3)\ 2H^{\cdot} + X'' \rightleftharpoons H_2X.$$

Silver chloride dissolves in solutions of ammonia, potassium cyanide and sodium thiosulphate owing to the formation of complex ions such as $Ag(NH_3)_2^{\cdot}$, $Ag(CN)_2'$ and AgS_2O_3'. The solubility of lead sulphate in a solution of ammonium acetate is usually explained in a similar way, the formation of complex ions such as $Pb(SO_4)_2''$ being assumed; but recent investigations indicate that the effect is rather to be ascribed to the fact that lead acetate shews an abnormally small degree of ionisation in solution (and still smaller in presence of ammonium acetate); it is the tendency to form these molecules which determines the change in question:—

$$Pb^{\cdot\cdot} + 2CH_3CO_2' \rightleftharpoons 2Pb(CH_3CO_2)_2.$$

The properties and reactions of most salts in dilute aqueous solution belong, according to this hypothesis, principally to the ions; barium chloride, for example, gives the reactions of chloride ions with silver salts and of barium ions with sulphates, and these reactions are given equally well with all other metallic chlorides or barium salts respectively. The colour of salts in aqueous solution is similarly ascribed to the ions, $Cu^{\cdot\cdot}$ being blue, $Fe^{\cdot\cdot}$ and $Ni^{\cdot\cdot}$ green, $K^{\cdot}$ and $Na^{\cdot}$ colourless, MnO_4'' green, MnO_4' pink, CrO_4'' yellow, Cr_2O_7'' orange, and so on.

Solutions of double salts, such as the alums, behave qualitatively as the two salts separately, potash alum for example shewing the reactions of the ions $K^{\cdot}$, $Al^{\cdot\cdot\cdot}$ and SO_4'', whereas the complex single salts such as the ferrocyanides, ferricyanides, cobalticyanides and chromoxalates for the most part shew no reactions of the metal or acid radicle which their names appear, at first sight, to indicate; *e.g.* ferrocyanides in solution do not shew the reactions of either Fe or CN ions. The distinction however between these two classes of salts is not by any means well defined; potassium ferrioxalate for example contains, in solution, ferric and oxalic ions as well as ferrioxalic ions; it would appear, in fact,

that the complex ions of the single salts tend to dissociate into the simpler constituents, a state of equilibrium being reached—complex single salt $\rightleftarrows$ simple double salt—

$$e.g.\ 2K_3[Fe(C_2O_4)_3] \rightleftarrows 3K_2C_2O_4 . Fe_2(C_2O_4)_3,$$

but that the degree of such dissociation is very variable in the different cases.

The solutions of the various reagents usually supplied in laboratories are made up of various arbitrary strengths, and the strength of the solution to be examined is also as a rule unknown or only roughly estimated. Hence it is obviously necessary to add each reagent tentatively, drop by drop, until no further effect is produced, making careful note of the intermediate changes (colour effects, redissolving of precipitates &c.); excess of the reagent is, in most cases, then added for the reason given above.

The solution of the substance prepared according to the instructions on page 46 is examined for metals according to the following tables. If only one metal is present the special tests are made with portions of the original solution; if more than one metal is present the characteristic reactions of one may interfere with those of another, so that in this case separation becomes necessary. The special tests are then applied to the solutions obtained by dissolving the various precipitates in appropriate solvents. Otherwise there is no essential difference between the method of analysing for one or many metals.

Hydrochloric acid precipitates silver, mercury when in the mercurous state, and lead as chlorides $AgCl$, $HgCl$ and $PbCl_2$. [The latter being somewhat soluble even in cold water may not be precipitated if the solution is very dilute.] The chlorides of all the other common metals being easily soluble will remain in solution. Bismuth and antimony are often precipitated here as oxychlorides ($BiOCl$, $SbOCl$), but the precipitate, in these cases, dissolves at once on further addition of HCl. If the HCl used as precipitant is fairly concentrated it may cause the separation of certain other chlorides (notably $BaCl_2$) owing to the influence of the common ion*, as explained above; these easily redissolve on addition of cold water.

The filtrate obtained after separation of the above chlorides is now saturated with hydrogen sulphide gas, when mercury (mercuric), lead, bismuth, copper, cadmium, arsenic, antimony and tin are precipitated as sulphides HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, Sb_2S_3 or Sb_2S_5, SnS or SnS_2.

Under ordinary conditions arsenic compounds are first reduced to the arsenious state with separation of sulphur:

$$As_2O_5 + 2H_2S = As_2O_3 + 2H_2O + 2S,$$

arsenious sulphide As_2S_3 being afterwards precipitated. The first change takes place very slowly requiring repeated boiling and saturation with H_2S, and for this reason arsenic in this state is often overlooked. The precipitation may be greatly hastened by first boiling the solution with SO_2 to reduce the arsenic compound before passing H_2S: the excess of SO_2 being of course first removed owing to its action on H_2S; it must be remembered also that complication may arise owing to the fact that sulphuric acid is produced in the

---

* Recent experiments of Thorne (*Am. Journ. of Science*, 1905, 441) make it doubtful whether the explanation is satisfactory in this case.

reducing action of SO_2 and consequently that sulphates of Ba, Pb &c. may be precipitated. Under certain conditions As_2S_5 may be precipitated from arsenic compounds by H_2S, but in general the concentration of $As^{\cdot\cdot\cdot\cdot\cdot}$ ions is too small owing to the feebly basic nature of arsenic in the pentavalent state.

A precipitate of sulphur on passing H_2S indicates generally the presence of an oxidising agent such as strong nitric acid, chlorine, bromine, iodine, permanganates, bichromates, ferric salts &c.

[*e.g.* $H_2S + O = H_2O + S$, $H_2S + Cl_2 = 2HCl + S$.]

In such cases the solution often shews a marked colour change, bichromates changing from orange to green and pink permanganate solutions becoming colourless.

The precipitate produced by H_2S is well washed, to remove the salts and free acids remaining in solution, and is then digested with yellow ammonium sulphide*. This converts the sulphides of arsenic, antimony and tin into soluble sulpho-salts, such as

$$(NH_4)AsS_2,\ (NH_4)SbS_2 \text{ and } (NH_4)SnS_3—$$
$$As_2S_3 + (NH_4)_2S = 2(NH_4)AsS_2.$$

Stannous sulphide does not dissolve in colourless ammonium sulphide; in polysulphides however it dissolves, taking up sulphur to form the corresponding stannic compound. In a similar way yellow ammonium sulphide partially converts antimonious sulphide into the sulpho-salt corresponding to antimonic sulphide.

The precipitation of the above metals by H_2S in presence of HCl is generally incomplete, or may be prevented altogether, if the hydrochloric acid employed is too concentrated; this might be expected from the fact that many of these sulphides dissolve in concentrated HCl evolving H_2S, the reaction being reversible and depending upon the conditions. The action of hydrochloric acid upon antimonious sulphide is a good example:

$$Sb_2S_3 + 6HCl \rightleftharpoons 2SbCl_3 + 3H_2S.$$

In addition to the above-mentioned sulphides, those of Fe, Zn, Mn, Ni and Co also are nearly insoluble in water, yet they are not precipitated if free hydrochloric acid is present—at any rate under ordinary conditions of concentration &c. In presence of only free acetic acid ZnS, NiS and CoS separate practically completely and MnS not at all. FeS is partially precipitated at certain concentrations; and the precipitation is made more complete if a strong solution of sodium acetate is added; the latter will in fact cause the separation of FeS from a clear solution of ferrous acetate, acetic acid and H_2S.

The facts mentioned above are perhaps most easily interpreted in terms of the ionic dissociation hypothesis; precipitation of the sulphide MS will begin, as before indicated, when the product of the concentrations of the M and S ions exceeds the solubility value; in the case of the sulphides mentioned, the solubility product is small but is by no means the same for each sulphide. Starting with different salts, say chlorides, at the same (moderate) dilution, the concentration of the metallic ions will not generally vary much since salts are, as a rule, highly ionised; precipitation of the sulphide will therefore principally depend on the concentration of the S ions and on the solubility of the particular sulphide.

* For the composition of the ordinary yellow ammonium sulphide, see footnote page 10.

Hydrogen sulphide being a very weak acid, its ionisation* will be considerably increased by dilution, but will, on the other hand, be diminished if the concentration of $H^{\bullet}$ is increased, *e.g.* by adding strong HCl. Addition of sodium acetate by increasing the concentration of the anions $(CH_3CO_2)'$ will suppress, or lower the concentration of, the hydrogen ions with formation of slightly ionised acetic acid, and so allow greater ionisation of the H_2S.

Although the precipitation of sulphides by H_2S, or their solubility in acids, depends principally on the circumstances above mentioned, there are other conditions which have also to be taken into account. The sulphides of nickel and cobalt for instance are not dissolved to any extent by HCl even if concentrated, yet H_2S gives no precipitate in solutions of nickel or cobalt salts in presence of dilute HCl; the physical state of aggregation of the solids is probably here concerned. In the case of strong solutions the degree of ionisation of the metallic salt may be an important determining factor; the solubility of Sb_2S_3 in strong HCl, for example, depends not only on the lowering of the concentration of S'' by $H^{\bullet}$, but also, amongst other things, on the fact that $SbCl_3$ is only very little ionised in strong solution.

The filtrate from the H_2S precipitate is tested with more H_2S to ascertain whether the separation is complete; if this is the case the excess of H_2S is removed by boiling and a few drops of nitric acid are then added in order to convert any ferrous salt which may be present into the ferric state (since ferrous salts are only incompletely precipitated by ammonia). The nitric acid acts as an oxidising agent, becoming itself reduced to the state of nitric oxide

$$3FeCl_2 + HNO_3 + 3HCl = 3FeCl_3 + 2H_2O + NO.$$

A brown colour is often noticed on first addition of HNO_3; this is due to a compound of NO with unaltered ferrous salt and which is destroyed by heating. This has the variable composition xFeX.yNO and probably exists as a complex cation made up of Fe and NO.

Ammonium chloride and ammonia are now added; the result of this is that, from most of their salts, Fe''', Cr''' and Al''' are precipitated as hydroxides, *e.g.*

$$FeCl_3 + 3NH_3 + 3H_2O = Fe(OH)_3 + 3NH_4Cl,$$

if however the solution contains phosphoric acid they will be precipitated wholly or partially as phosphates $FePO_4$, $CrPO_4$, $AlPO_4$. In addition to the latter, many other salts which are insoluble (or nearly so) in water, but are soluble in HCl—such as phosphates of Ca, Sr, Ba, Mg, and oxalates (fluorides, silicates, borates &c.) of Ca, Sr, Ba—may be precipitated here, the change being usually regarded as consisting merely in the neutralisation of the free HCl by the ammonia.

Phosphates of Zn, Mn, Ni and Co may also be partially precipitated in this group; they may be decomposed by digesting the precipitate with ammonium sulphide, thus:

$$Zn_3(PO_4)_2 + 3(NH_4)_2S = 2(NH_4)_3PO_4 + 3ZnS.$$

---

* First as $H^{\bullet} + (SH)'$ and further as $2H^{\bullet} + S''$.

The solution is tested for phosphate with magnesia mixture; its presence shews that the precipitate contained Zn, Mn, Ni, Co or Fe as phosphate. The residue, containing the resulting sulphide, is again dissolved in acids and treated as before with HNO_3, NH_4Cl and NH_3; the precipitate so obtained is now free from Zn, Mn, Ni and Co, which may be looked for separately in the filtrate.

The separation of groups III. and IV. by means of NH_4Cl and NH_3 is sometimes very imperfect; manganese and zinc especially, and sometimes nickel and cobalt, are often carried down to some extent in the third group even though phosphates are absent. It is therefore necessary, in cases of accuracy, to redissolve the precipitate in HCl and again precipitate with NH_4Cl and NH_3, repeating the operations if necessary.

A more complete separation of Fe''', Cr''', Al from Zn, Mn, Ni, Co is effected by means of barium carbonate which precipitates only the former metals; the process takes some time, but is advisable when accuracy is required, especially if traces of Zn have to be looked for.

If much chromium is present, zinc, if present in small proportion, might be entirely carried down by the ammonia. Hence in this case it is advisable to convert the chromium into chromate by oxidation, *e.g.* with sodium peroxide.

The precipitating agent in this group is, of course, the ammonia—or ammonium hydroxide, as its aqueous solution is usually regarded.

The principal object of adding ammonium chloride is to prevent the precipitation of the hydroxides of Mg and Mn by the ammonia; it also has the effect of rendering the precipitation of aluminium hydroxide more complete. The latter circumstance is probably explained by the fact that the aluminium hydroxide dissolves to some extent in water, forming a colloidal solution (hydrosol) which is changed by salts to the insoluble form (hydrogel).

Mg, Mn, Zn, Ni and Co salts all give incomplete precipitates of their hydroxides (or basic salts) with ammonia alone, those of Zn, Ni and Co being soluble in excess owing to formation of complex cations $MxNH_3$. In presence of ammonium chloride, however, ammonia causes no precipitation in any of these cases.

The hydroxides of these metals are very nearly insoluble in water, $Mg(OH)_2$ being just sufficiently soluble for its solution to shew alkalinity with certain indicators. Precipitation of the hydroxide will tend to begin when the product of the concentrations of the metallic and hydroxyl ions (M and $(OH)^2$) reaches the critical value, or solubility product.

$$[M^{\cdot\cdot} + 2OH' \rightleftharpoons M(OH)_2.]$$

Ammonium hydroxide is a weak base, *i.e.* its aqueous solution is comparatively little ionised, $[NH_4OH \rightleftharpoons NH_4^{\cdot} + OH']$; it also decomposes in part into NH_3 and H_2O. For these reasons the concentration of the OH ions is small. With the considerable concentration of the metallic ions present however the value of the solubility product of the metallic hydroxide will, in general, be reached and precipitation occur. But if a sufficiently concentrated solution of an ammonium salt, such as ammonium chloride, is added the concentration of OH' will be lowered by the increased concentration of $NH_4^{\cdot}$ and the solubility product of the metallic hydroxide may not be reached. [Compare this 'suppression' of OH' by $NH_4^{\cdot}$ with that of $H^{\cdot}$ by (CH_3CO_2') on page 68.]

But in preventing the precipitation of hydroxides by ammonia, ammonium chloride may be instrumental in another way. It is well known that the chlorides of these metals form with ammonium chloride compounds which are empirically represented as $MCl_2 xNH_4Cl$; these may exist, in part at any rate, as *single* salts of complex anions such as MCl_4'' or of complex cations $MxNH_3^{\cdot\cdot}$, and only partially as simple double salts, so that the concentration of the ion $M^{\cdot\cdot}$, as such, is therefore diminished.

In the general scheme for the analytical separation of metals, many prefer to add ammonium sulphide in addition to ammonium chloride and ammonia, without first filtering off the precipitate produced by the ammonia. The joint result of this precipitation is then classified as the Third Group; it will contain Fe″, Zn, Mn, Ni, Co as sulphides, and the remainder as hydroxides, phosphates &c. These are then further separated by the methods above mentioned.

This method of procedure has the advantage of giving in many cases a more complete precipitation and it also obviates the difficulty, referred to above, with regard to the phosphates of Zn, Mn, Ni, Co, which in this way are converted into sulphides. It must be remembered, however, that the ammonium phosphate resulting from the decomposition of phosphates of Fe, Zn, Mn, Ni, Co with ammonium sulphide may react with salts (chlorides &c.) of Ca, Sr, Ba, Mg, converting them into phosphates and so including them in this group, when otherwise they would have occurred normally in groups V. and VI.

Another slight disadvantage of this joint precipitation method is that the filtrate to be examined for the future groups must of necessity contain ammonium sulphide; by the other method this is only necessary when Zn, Mn, Ni or Co are present (see note †† General Table, p. 72).

To the filtrate from the ammonia precipitate ammonium sulphide is added; this precipitates Zn, Mn, Ni and Co as sulphides. In a solution of ammonium sulphide the concentration of S'', or $(SH)'$, ions is considerable, the salt being much ionised, and hence, under ordinary conditions, the solubility product of the metallic sulphide (or hydrosulphide) is greatly exceeded. [Here there are no $H^{\cdot}$ ions to diminish the concentration of S'' with formation of H_2S.]

Nickel sulphide dissolves to a considerable extent in yellow ammonium sulphide giving a dark brown solution; it is suggested that this may be due to the formation of the sulphide of a complex cation—perhaps $[Ni(NH_3)_6]S$; others consider that a colloidal solution of NiS is formed, and more recently the solubility has been ascribed to the formation of NiS_4. Colourless ammonium sulphide does not dissolve NiS in this way, especially if ammonium chloride is present, so that the solvent action can be avoided by passing H_2S into the ammoniacal solution containing much ammonium chloride, instead of using yellow ammonium sulphide. Otherwise it is necessary to acidify the dark brown solution (this precipitates NiS together with sulphur), filter, and again make the solution alkaline before proceeding to the next group.

It is well to remember that ammonium sulphide solution may possibly contain sulphate, due to oxidation, and this would precipitate Ba, &c.; the reagent should therefore be tested for sulphate before use.

To the filtrate from the last precipitate, still containing ammonium chloride and ammonia, ammonium carbonate is added. This precipitates the carbonates of Ca, Sr, Ba. The solution is warmed to decompose bicarbonates and carbamates (see page 20) of these metals, which are soluble; it must not be boiled however since, the action being reversible, ammonium chloride tends to redissolve the precipitate with formation of volatile ammonium carbonate—

$$CaCO_3 + 2NH_4Cl \rightleftharpoons CaCl_2 + (NH_4)_2CO_3.$$

The hydroxides of Ca, Sr and Ba, although sparingly soluble in water, are not precipitated by ammonia even in absence of ammonium chloride, although they are partially precipitated by caustic potash or soda.

The solubilities being greater than those of the hydroxides referred to in the previous sections, a greater concentration of OH' is required, other things being equal, to attain the value of the solubility product, and the small concentration of OH' in the ammonia solution is never sufficient.

The carbonates of Ca, Sr, Ba are scarcely soluble and are precipitated when a soluble carbonate is added to a solution of their salts. [Mg is also precipitated as a basic carbonate; in presence of ammonium chloride, however, it is not precipitated owing to the formation of the complex ions (see above).] *Free* carbonic acid does not precipitate the carbonates from the ordinary salts of these metals in neutral solution since the concentration of CO_3'' is here very small, H_2CO_3 being a very weak acid.

The solution remaining, after separation of the foregoing metals, contains now only magnesium, potassium, sodium and ammonium; it is examined according to Table VI. Ammonium, having been added in the reagents employed, must of course be examined for separately in the original solution.

GENERAL TABLE FOR MIXTURES OF METALS.

SEPARATION INTO GROUPS.

The solution prepared according to the directions on page 52 is examined as follows:

(1)	(2)	(3)§	(4)	(5)‖‖
Add *Hydrochloric Acid* (dil.). Ppt. = {SILVER, LEAD, MERCURY (monad)} Filter. Examine ppt. by Table I. and solution by column (2) A ppt. which redissolves easily in excess of HCl is probably due to Antimony or Bismuth. One which redissolves at once in cold water, is probably a Barium salt.	Pass *Hydrosulphuric Acid* gas to saturation, and heat*. Ppt. † = {MERCURY (dyad), LEAD, BISMUTH, COPPER, CADMIUM} A; {ARSENIC, ANTIMONY, TIN} B Filter. Examine filtrate by column (3). Wash ppt. well and digest it for some time with hot yellow ammonium sulphide‡. Filter. RESIDUE (A) Examine by Table II. A. | SOLUTION (B) Examine by Table II. B.	Boil till H_2S is entirely expelled. Add nitric acid drop by drop as long as any change occurs‖. Then add NH_4Cl and *ammonia* till alkaline. Boil¶. Ppt. ** = {IRON, ALUMINIUM, CHROMIUM} Hydroxides or Phosphates; {Barium, Strontium, Calcium, Magnesium} Phosphates; {Calcium, (Strontium, Barium)} Oxalates (or Fluorides); Sometimes Manganese and Zinc in small quantities. Filter. Examine filtrate by column (4) and ppt. by Table III.	Add *Ammonium Sulphide* in slight excess and heat††. Ppt. §§ = {ZINC, MANGANESE‡‡, NICKEL, COBALT} Filter. Examine filtrate by column (5) and ppt. by Table IV.	Add *Ammonium Carbonate* and heat gently. Ppt. = {BARIUM, STRONTIUM, CALCIUM} Filter. Examine filtrate by Table VI. and ppt. by Table V.

* If much acid has been added, the solution should be diluted largely with water, or nearly neutralised, before passing H_2S. If a further pptn. occurs on heating, boil and pass H_2S again.

† A white or nearly white ppt. which does not settle is probably *sulphur*, shewing the presence of an oxidising agent. If the solution turns bright green with pptn. of sulphur, chromic acid is probably present.

‡ Since CuS is somewhat soluble in yellow ammonium sulphide, it is advisable to use *sodium* sulphide if traces of Cu are being looked for.

§ Test a portion of this solution by evaporating to dryness and heating the residue. A residue which does not dissolve in HCl on heating is probably SILICA. If present, it must be removed from the remainder of the solution in the same way before proceeding. If the residue blackens considerably on heating, organic bodies such as sugar or tartaric acid are probably present. These should be destroyed by ignition, since they prevent the precipitation of this group, wholly or in part.

‖ From a solution of an iodide strong nitric acid will cause the separation of iodine which may be partly precipitated; that which remains in solution is either vaporised or oxidised on boiling.

¶ If complete separation is required, the ppt. produced by ammonia must be redissolved in HCl and reprecipitated by NH_4Cl and NH_3, and this process repeated until the filtrate gives no ppt. with ammonium sulphide. In presence of chromium it is necessary to boil for a considerable time to ensure its precipitation with ammonia.

** Phosphates of zinc, manganese, nickel and cobalt may also be precipitated here, in part. If it is required to look for them, the ammonia ppt. must be washed and digested with ammonium sulphide, the filtrate tested for phosphate, and the ppt. washed and redissolved in HCl (with a drop of HNO_3 if necessary) and treated as in column (3). It is the safest plan always to treat the precipitate in this manner.

†† It is advisable to test a few drops of the filtrate with ammonium sulphide before adding it to the main portion.

‡‡ If a large excess of ammonia is present, manganese may be entirely held in solution, until the solution is boiled for some time.

§§ Possibly also some IRON, if much alkaline phosphate is present, since ferric and aluminium phosphates are only imperfectly precipitated in this case.

‖‖ If the filtrate from the ammonium sulphide ppt. is dark coloured (probably indicating nickel), the solution should be acidified with dilute HCl, boiled, filtered, and again rendered alkaline with NH_3, before proceeding.

TABLE I. [First Group.]

Ag, Pb, Hg′.

Wash ppt. with cold water, then boil it for some time with a considerable quantity of hot water.

Filter

Residue Digest with ammonia. Filter.		Solution
Residue (black) MERCURY. Confirm by drying ppt. at gentle heat, mixing with dry Na_2CO_3 and heating in a bulb-tube. Grey ring, united into globules by rubbing with a rod.	Solution Acidify with HNO_3, white ppt. turning violet on exposure to sunlight. SILVER.	Add potassium chromate. Yellow ppt. insoluble in acetic acid. LEAD.

The precipitate produced by hydrochloric acid contains silver, lead, and mercurous chlorides AgCl, $PbCl_2$, HgCl.

The separation of these is based upon the fact that

(1) $PbCl_2$ is soluble in boiling water, AgCl and HgCl insoluble.

(2) AgCl is soluble in ammonia, HgCl insoluble.

The $PbCl_2$ is first extracted with boiling water, and confirmatory tests for lead applied to the solution so obtained.

The AgCl is extracted from the residue by ammonia, this dissolves it, forming the chloride of a complex cation $(Ag\,x NH_3)$. Nitric acid decomposes this, reprecipitating AgCl.

HgCl is converted by ammonia into a black substance, which remains undissolved, and is confirmed by the dry test for mercury. This black substance is sometimes regarded as the chloride of dimercurous ammonium $(NHg_2'H_2)Cl$, but it appears probable that it is in reality a mixture of metallic mercury with the mercuric-ammonium compound

$$Hg + (NHg''H_2)Cl.$$

TABLE II. A. [SECOND GROUP A.]

Hg″, Pb, Bi, Cu, Cd.

Wash well. Heat with moderately dilute nitric acid as long as any action is observed.

FILTER

<table>
<tr>
<td rowspan="3">RESIDUE (black *)
MERCURY (mercuric)
Confirm by drying at a gentle heat, mixing with dry Na_2CO_3 and heating in a bulb-tube.
Grey ring, united into globules by rubbing with a rod.</td>
<td colspan="3">SOLUTION
Add dilute H_2SO_4 and an equal volume of alcohol †.
FILTER</td>
</tr>
<tr>
<td rowspan="2">White ppt.
LEAD.
Confirm by dissolving the ppt. in ammonium acetate and adding potassium chromate.
Yellow ppt. sol. in NaOH.</td>
<td colspan="2">Boil off the alcohol. Add ammonia in excess.
FILTER</td>
</tr>
<tr>
<td>Ppt.
Dissolve in the least possible quantity of HCl.
Add much water.
White milky ppt.
BISMUTH.</td>
<td>Solution.
If blue contains COPPER.
Confirm by acidifying a portion with acetic acid and adding potassium ferrocyanide. Chocolate ppt.
If copper is present, add KCN to the remainder of blue solution until colourless. Pass H_2S.
Yellow ppt.
CADMIUM ‡.</td>
</tr>
</table>

* It is best to heat the ppt. with water and add strong HNO_3 drop by drop till the action commences. If the acid be too strong, lead will be chiefly converted into sulphate and remain in the residue with mercury. The latter may also be converted into a white substance.

† It is advisable to test a small portion for lead in the first instance, since, if absent, sulphuric acid and alcohol need not be added to the remainder.

‡ Under certain conditions, an orange precipitate of dithiooxamide $C_2H_4N_2S_2$ may be obtained here. See Wöhler and Hirschberg, *Ber.* 1910, 753.

EXPLANATION OF TABLE II. A.

The residue insoluble in ammonium sulphide contains mercury, lead, bismuth, copper and cadmium, as sulphides.

Their separation is based upon the following principles:

(1) HgS is insoluble in nitric acid*. The remaining sulphides dissolve with separation of sulphur, *e.g.*:

$$3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 4H_2O + 2NO + 3S.$$

(2) Dilute sulphuric acid precipitates lead as sulphate (more completely in presence of alcohol), leaving Bi, Cu and Cd in solution.

(3) Ammonia throws down bismuth as hydroxide $Bi(OH)_3$ (or a basic salt) which is insoluble in excess. Copper and cadmium are in the first instance precipitated (as basic salt and as hydroxide respectively) but dissolve at once in excess of ammonia, forming the complex cations $(Cu4NH_3)^{\cdot\cdot}$ (dark blue) and $(CdxNH_3)$ (colourless).

Bismuth hydroxide dissolves in hydrochloric acid, forming the chloride $BiCl_3$; this is easily hydrolysed by water, forming the insoluble basic salt or oxychloride. Since this reaction is reversible, *i.e.* since the oxychloride is soluble in hydrochloric acid, it is necessary to avoid using excess of acid in dissolving the hydroxide

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl.$$

(4) The separation of the two remaining metals, copper and cadmium, from one another may be effected in two different ways, which depend upon the following properties:

(*a*) Potassium cyanide first precipitates the cyanides of both metals:—$Cu(CN)_2$, which immediately loses cyanogen becoming $CuCN$, and $Cd(CN)_2$. These precipitates readily dissolve in excess; the solution so formed contains the copper almost entirely in the form of the complex anion $(Cu(CN)_2)'$ and scarcely at all as the double salt $KCN.CuCN$; the cadmium however exists partly as ions of the double salt $2KCN.Cd(CN)_2$, and partly as the complex anion $(Cd(CN)_4)''$ (the latter being less stable than the copper complex). Hence the solution contains a notable concentration of $Cd^{\cdot\cdot}$ ions, and scarcely any $Cu^{\cdot}$ ions and, on addition of S'' (by passing H_2S), CdS is precipitated, but the solubility product of copper sulphide is not reached, notwithstanding the greater solubility of CdS.

(*b*) Owing to the greater solubility of cadmium sulphide in water, the two sulphides may be separated by digestion with boiling dilute sulphuric acid; the concentration of $H^{\cdot}$ is here sufficient to 'suppress' the S'' (as H_2S) below the value required, with $Cd^{\cdot\cdot}$, to reach the critical value for cadmium sulphide but not for copper sulphide.

Cadmium may also be separated from copper by boiling the solution with caustic alkali in presence of a tartrate. Cadmium is precipitated but not copper, the latter remaining in solution as a complex ion.

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* Some prefer to use strong nitric acid, in which case the lead is converted into sulphate and remains in the residue with HgS; the latter is often converted into a white $Hg(NO_3)_2.2HgS$ which by long boiling is dissolved as mercuric nitrate. Or the residue may be digested with a strong solution of ammonium acetate which dissolves only $PbSO_4$.

TABLE II. B. [Second Group B.] Method 1.

Acidify with dil. HCl. Filter. Neglect filtrate. (If ppt. is nearly white and does not settle, it is probably only sulphur, and may be neglected.)

Wash ppt. and digest it for some time with warm ammonium carbonate*.

<table>
<tr><th colspan="3">Filter</th></tr>
<tr><th>Solution</th><th colspan="2">Residue</th></tr>
<tr><td rowspan="3">Acidify with HCl.
Yellow ppt.—probably
ARSENIC†.
Confirm by dissolving ppt. in an ammoniacal solution of H_2O_2 and adding magnesia mixture. A crystalline precipitate of $MgNH_4AsO_4$ is formed on stirring, or in dilute solutions on standing‡.
[Some Tin may also be present in this ppt. To confirm it, roast ppt. in open vessel, and fuse residue with KCN. Metallic Sn remains, which when dissolved in HCl gives white ppt. with $HgCl_2$.]</td><td colspan="2">Wash. Heat with strong HCl. Filter if necessary. (Residue is only S and traces of As_2S_3.) Heat gently to remove H_2S. Divide solution into two parts.</td></tr>
<tr><th>1.</th><th>2.</th></tr>
<tr><td>Test for Sn.
Dilute and add a small piece of zinc. Allow to stand. Pour off clear solution. Dissolve residue in strong hot HCl. Add $HgCl_2$. White ppt. often turning grey.
TIN†.</td><td>Test for Sb.
Pour the solution on to a piece of zinc on platinum foil. Black stain on the platinum.
ANTIMONY†.
Confirm by dissolving stain off in ammonium sulphide, and gently evaporating the solution.
Orange residue if Sb is present.</td></tr>
</table>

* Preferably *sequi*-carbonate, saturated in the cold. Instead of ammonium carbonate, strong boiling HCl may be used, in which case Sn and Sb dissolve as chlorides, while As_2S_3 remains insoluble.

† Ascertain, if possible, whether *-ous* or *-ic* (or both) in original solution.

‡ Or by heating in a bulb-tube with dry Na_2CO_3, and charcoal or KCN. Another method is to heat the precipitate with a solution of caustic soda and metallic zinc, and test the evolved gas for arseniuretted hydrogen by means of silver nitrate.

EXPLANATION OF TABLE II. B. METHOD 1.

The solution after digestion of the mixed sulphides with yellow ammonium sulphide contains arsenic, antimony, and tin, as sulpho-salts.

These are decomposed by dilute HCl, the insoluble sulphides being reprecipitated, *e.g.*

$$\underset{\text{soluble ammonium sulpharsenite}}{(NH_4)_2S \, . \, As_2S_3} + 2HCl = \underset{\text{insoluble arsenious sulphide}}{As_2S_3} + 2NH_4Cl + H_2S.$$

Tin will always be reprecipitated as yellow stann*ic* sulphide, since stannous sulphide is converted into stannic by the excess of sulphur in the yellow ammonium sulphide.

[A *white* ppt. is merely sulphur from the yellow ammonium sulphide, *e.g.*

$$(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S.]$$

The ppt. (As_2S_3 (or As_2S_5), Sb_2S_3 (or Sb_2S_5), SnS_2 and free S) is washed till free from HCl, and digested with warm ammonium carbonate.

As_2S_3 dissolves; the reaction may be approximately represented thus—

$$4As_2S_3 + 4(NH_4)_2CO_3 = \underset{\text{soluble arsenite}}{(NH_4)_2O \, . \, As_2O_3} + \underset{\text{soluble sulpharsenite}}{3\{(NH_4)_2S \, . \, As_2S_3\}} + 4CO_2.$$

Sb_2S_3 (and Sb_2S_5) are practically insoluble, and SnS_2 very slightly soluble.

The solution of arsenite and sulpharsenite is acidified with HCl, which precipitates the arsenic as As_2S_3.

$$(NH_4)_2O \, . \, As_2O_3 + 3\{(NH_4)_2S \, . \, As_2S_3\} + 8HCl = 4As_2S_3 + 8NH_4Cl + 4H_2O.$$

Arsenic is confirmed in this precipitate, by dissolving it in ammonia together with peroxide of hydrogen—

$$As_2S_3 + 12NH_3 + 14H_2O_2 = 2(NH_4)_3AsO_4 + 3(NH_4)_2SO_4 + 8H_2O,$$

and confirming the resulting arsenate with magnesia mixture.

The residue insoluble in ammonium carbonate, containing the antimony and tin, is dissolved in strong hot HCl. SnS_2 dissolves, forming $SnCl_4$; Sb_2S_3 and Sb_2S_5 both form $SbCl_3$ (the latter with separation of S); H_2S being evolved.

Sulphur and traces of As_2S_3 remain undissolved.

The HCl solution is divided into two parts.

One is examined for tin, by adding zinc. This precipitates tin as metal,

$$SnCl_4 + 2Zn = Sn + 2ZnCl_2.$$

The deposited tin is dissolved in HCl, which converts it into stann*ous* chloride $SnCl_2$, and mercuric chloride added. This is reduced first to white mercurous chloride, and afterwards, if sufficient stannous salt be present, to grey metallic mercury,

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4$$

and

$$2HgCl + SnCl_2 = 2Hg \quad + SnCl_4.$$

The other part is examined for antimony by causing the solution to act upon zinc in contact with platinum foil. Antimony is deposited as metal on the platinum. On digesting with yellow ammonium sulphide, antimony dissolves as a sulpho-salt, and on evaporation of the solution, orange antimony sulphide remains.

TABLE II. B. [SECOND GROUP B.] METHOD 2.

Acidify with HCl (dil.). Filter. Neglect filtrate. (If ppt. is nearly white, and does not settle, it is probably only sulphur, and may be neglected.)

Wash ppt. and dissolve it in strong HCl (with a drop of HNO_3, or a crystal of $KClO_3$, if necessary). Heat gently to expel chlorine, &c. Reserve a portion. Introduce remainder into a vessel in which hydrogen is being generated by the action of Zn and dil. H_2SO_4.

Pass the evolved gases through a wash-bottle containing solution of lead acetate, and then into a strong solution of silver nitrate. A black ppt. indicates As or Sb.

FILTER

<table>
<tr><td rowspan="2">SOLUTION
Add a few drops of $AgNO_3$ and then dilute ammonia, drop by drop. Yellow ppt. where the liquids meet.
ARSENIC.</td><td colspan="2">PPT.
Wash well. Digest with hot tartaric acid on the filter.</td></tr>
<tr><td>SOLUTION
Add HCl dil. and pass H_2S. Orange ppt.
ANTIMONY.</td><td>RESIDUE neglect</td></tr>
</table>

Examine the other portion of the solution for tin by diluting, adding a small piece of zinc and allowing to stand. Pour off clear solution. Boil residue with strong HCl. Add $HgCl_2$. White ppt. often turning grey, TIN.

EXPLANATION OF TABLE II. B. METHOD 2.

This method is based upon the fact that compounds of arsenic and antimony when brought in contact with zinc and dilute acid (HCl or H_2SO_4), evolve gaseous arsenic and antimony trihydrides, AsH_3 and SbH_3. (A portion of the As and Sb being usually precipitated on the Zn.)

The gases are purified from any H_2S which may be present by passing through a solution of lead acetate, and then led into a solution of silver nitrate. This decomposes them as follows:—

$$AsH_3 + 6AgNO_3 + 3H_2O = \underset{\text{Black ppt.}}{6Ag} + \underbrace{H_3AsO_3 + 6HNO_3}_{\text{in solution}}$$

$$SbH_3 + 3AgNO_3 = \underset{\text{Black ppt.*}}{SbAg_3} + 3HNO_3.$$

The solution therefore contains arsenious acid, nitric acid, and excess of silver nitrate. On carefully neutralising with ammonia, yellow silver arsenite Ag_3AsO_3 is precipitated. (This ppt. being soluble either in HNO_3 or NH_3, exact neutralisation is necessary.)

The residue on the filter consists of metallic silver, and silver stibide Ag_3Sb. Tartaric acid dissolves Sb leaving Ag, and on passing H_2S into the solution, Sb_2S_3 is obtained as an orange precipitate. The Tin is found as in Method 1.

Amongst other alternative methods of separating As, Sn, Sb the following may be mentioned:—

(a) The sulphides are dissolved in fuming nitric acid; the solution is evaporated to remove excess of acid, and is then mixed with a moderately strong solution of caustic soda and alcohol. Antimony is precipitated as $Na_2H_2Sb_2O_7$; tin and arsenic remaining in solution as stannate and arsenate, are again obtained as sulphide, and separated as in Method 1.

(b) The sulphides are dissolved in caustic soda and the solution is boiled with sodium peroxide; on addition of excess of ammonium chloride and boiling, stannic hydroxide is precipitated. The arsenic and antimony remaining in solution are separated by acidifying and passing H_2S in the cold when only antimony is precipitated, which can be identified as in Method 1. Antimony may also be separated from tin by the oxalic acid method; the solution of the chlorides (after separation of arsenic by HCl) is made just alkaline with ammonia, excess of oxalic acid is added, the solution boiled and H_2S passed. Sb_2S_3 is pptd. and tin remains in solution. A similar result may be obtained by using strong phosphoric acid in place of oxalic acid.

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* This is perhaps a mixture of metallic silver with $Sb(OH_3)$.

TABLE III. [Third Group.]

Ppt. may contain Al, Fe, Cr, as hydroxides or phosphates; Ca, Ba, Sr, Mg, as phosphates; Ca(Ba, Sr) as oxalates (fluorides, borates)*. [Sometimes also Mn, Zn, Ni, Co; see Note (**) General Table, p. 72, also explanation, pages 68 and 69.]

Wash ppt. thoroughly and examine portions of it as follows:—

1. Dissolve a small portion in HNO_3, add ammonium molybdate in considerable excess and heat. Yellow ppt. indicates PHOSPHATE†.

2. Fuse a portion of the ppt. with Na_2CO_3 in excess and a little KNO_3 on platinum foil‡. Yellow mass indicates CHROMIUM; confirm by extracting the fused mass with water, acidifying with acetic acid and adding lead acetate. Yellow ppt. $= PbCrO_4$.
Blue-green mass indicates MANGANESE; [this may mask the colour given by chromium, in which case add a few drops of alcohol and boil before applying confirmation test for Cr].

Dissolve the main portion of the ppt. in the least quantity of HCl and examine portions of the solution as follows:—

1. Dilute a portion with water and add potassium ferrocyanide. Blue ppt. indicates IRON§.

2. To another portion add caustic soda‖ in considerable excess, boil and filter. Neglect ppt. and to the filtrate add excess of ammonium chloride and boil. White gelatinous ppt. (often taking time to aggregate) indicates ALUMINIUM as hydroxide or phosphate (or both). Wash this ppt. and examine it for phosphate as above.

3.¶ To the main portion of the solution add a little acetic acid and a strong solution of sodium acetate in excess.

Filter

Ppt.	Solution
Phosphates of Al, Fe, Cr. Confirm by the above special tests. Oxalates of Ca(Ba, Sr). Confirm by heating to low redness and adding acetic acid, effervescence indicates OXALATE. Test resulting solution for Ca, &c. by Table V. and residue for Fluorides by heating with concentrated H_2SO_4.	Add $FeCl_3$ drop by drop; a yellowish-white ppt. indicates PHOSPHATE, which must have been present in the original ppt. in combination with Ca, Ba, Sr, Mg. If $FeCl_3$ gives a ppt., continue to add it until the solution is red, dilute if necessary, boil for some time and filter hot. Neglect ppt. (ferric phosphate and basic acetate) and examine filtrate for Ca, Ba, Sr, Mg by Tables V. and VI.

* Oxalates will have been destroyed if the solution has previously been evaporated, and the residue heated, to remove silica. Borates and fluorides are only imperfectly precipitated in this group, so that metals will probably be detected as usual in Group V.

† Arsenate would give a similar reaction if not previously separated in Group II.

‡ Or carefully add sodium peroxide or potassium percarbonate till strongly alkaline, and boil. The resulting yellow solution of chromate is tested as above, or it may be acidified with dil. H_2SO_4 and tested with H_2O_2 and ether. Manganese will not be indicated if this method is adopted. Test another portion of the solution for Al.

§ Ascertain by special tests in the *original* solution whether ferrous or ferric.

‖ The caustic soda supplied may contain Al or Si as impurity; hence it is advisable to make a blank test with the reagent alone and compare the results. If much chromium has been indicated it is advisable to convert it into the state of chromate (see previous note) before testing for aluminium and before separating phosphates.

¶ This section may of course be omitted if phosphates, oxalates (fluorides, borates) are absent (see note *).

EXPLANATION OF TABLE III.

Since the presence of phosphates renders the analysis of this group more complex, it is advisable to test a portion of the precipitate for phosphate in the first instance by dissolving it in nitric acid, adding considerable excess of ammonium molybdate and heating. [For the composition of the yellow precipitate of 'ammonium phosphomolybdate' see page 30.]

Fusion of the precipitate with sodium carbonate in presence of air (or of some oxidising agent such as KNO_3) converts the lower oxides of chromium and manganese into a chromate and manganate respectively, *e.g.*:—

$$Cr_2O_3 + 2Na_2CO_3 + 3O = \underset{\text{yellow mass}}{2Na_2CrO_4} + 2CO_2,$$

$$MnO + Na_2CO_3 + 2O = \underset{\text{green mass}}{Na_2MnO_4} + CO_2.$$

The fused mass is extracted with water to dissolve out the chromate, the manganate being generally decomposed in the process [if sufficient Mn is present however, the green solution formed will turn pink on acidification owing to formation of permanganate]. In presence of much Mn it is advisable to add a few drops of alcohol and boil, reduction then taking place with precipitation of an intermediate oxide such as $Mn_2O_3 . xH_2O$. After filtration the yellow solution is acidified with acetic acid and the chromate confirmed by addition of lead acetate, which precipitates yellow $PbCrO_4$.

[Boiling with sodium peroxide has a similar effect, but the manganese is not then indicated, being left in the residue with iron &c.]

The remainder of the precipitate is dissolved in hydrochloric acid. This converts the hydroxides into chlorides

$$M(OH)_3 + 3HCl = MCl_3 + 3H_2O,$$

the oxalates and phosphates dissolving potentially unchanged.

In terms of the ionic dissociation hypothesis these changes may be explained as follows: the hydroxides in question are not absolutely insoluble in water and give a solution containing some $M(OH)_3$ in equilibrium with the solid and also with its ions $M^{\cdot\cdot\cdot}$ and $3OH'$ [see page 65]. Addition of hydrogen ions (by adding an acid) removes the OH' as non-ionised HOH; more of the dissolved $M(OH)_3$ therefore ionises to restore equilibrium and therefore, for a similar reason, more solid dissolves; these changes continue until all is dissolved.

The phosphates and oxalates dissolve in HCl for a similar reason, but the slightly ionised product is here the weak acid instead of HOH. The weaker (less ionised) the acid the less will be the excess of HCl required to dissolve the salt.

A portion of the HCl solution is diluted and tested specially for iron with potassium ferrocyanide. To another portion an excess of caustic soda is added; this precipitates the whole group substantially in the same condition as before, but redissolves the aluminium hydroxide and phosphate with formation of sodium aluminate $xNa_2O . yAl_2O_3$. The aluminium,

which in the acid solution existed as the cation $Al^{'''}$, now goes to form anions; [the composition of the latter is not yet fully established but it is probable that they are univalent—such as AlO_2' or H_2AlO_3'—since the fact of dissolving aluminium in caustic alkali does not alter the freezing point of the solution].

Chromium hydroxide and phosphate dissolve in caustic soda for a similar reason but the solution is precipitated on diluting and boiling. If much chromium is present however, its separation in this way is difficult and it is then better to convert it entirely into the hexad (or chromate) form before proceeding. This can be done by fusing the precipitate with Na_2CO_3 in presence of air or other oxidising agent, or by boiling with sodium peroxide (see page 84). The resulting chromate remains in solution and does not interfere with the other tests.

Ferric phosphate when boiled with caustic soda is decomposed to a considerable extent giving the hydroxide and sodium phosphate; on long boiling this decomposition is nearly complete. (The phosphates of aluminium and chromium when reprecipitated from the soda solution also appear as mixtures of hydroxide and phosphate.)

The alkaline filtrate after boiling with excess of caustic soda is now tested for aluminium by boiling with excess of ammonium chloride. This precipitates the aluminium as hydroxide (or, if present originally as phosphate, as a mixture of hydroxide and phosphate). The decomposition of sodium aluminate by ammonium chloride may provisionally be written as:

$$Na_2O \cdot Al_2O_3 + 2NH_4Cl + 2H_2O = Al_2O_3 \cdot 3H_2O + 2NaCl + 2NH_3,$$

or in the 'ionic' form

$$H_2AlO_3' + NH_4^{\cdot} = Al(OH)_3 + NH_3,$$

the tendency being to form the molecules of the scarcely ionised aluminium hydroxide and ammonia or ammonium hydroxide.

To another portion of the original precipitate dissolved in hydrochloric acid excess of sodium acetate is added; the free hydrochloric acid is thus almost entirely converted into free acetic acid,

$$HCl + CH_3COONa = NaCl + CH_3COOH.$$

The phosphates of iron, chromium (and aluminium) and calcium oxalate and fluoride are soluble in hydrochloric acid but insoluble in acetic acid, whereas the phosphates of calcium, strontium, barium and magnesium dissolve both in acetic and hydrochloric acids; the former are therefore precipitated on adding sodium acetate. [Oxalates are confirmed by heating the precipitate to low redness, being thus converted into carbonates; fluorides evolve HF when acted upon by strong sulphuric acid, and the phosphates of iron and chromium and aluminium are confirmed by the special tests mentioned above.]

The acetic acid solution of the phosphates of Ca, Ba, Sr, Mg is now acted upon by ferric chloride which converts them into chlorides by double decomposition, ferric phosphate being precipitated,

$$Ca_3(PO_4)_2 + 2FeCl_3 = 2FePO_4 + 3CaCl_2.$$

If therefore a reddish white precipitate is obtained on addition of the first few drops

of ferric chloride, it proves that the phosphates of Ca, Ba, Sr or Mg were present. The ferric chloride is added in slight excess (indicated by the red colour of ferric acetate), and the excess of iron is then removed by boiling the solution; ferric acetate then undergoes partial hydrolysis, giving an insoluble basic salt $x\mathrm{Fe(CH_3CO_2)_3} \cdot y\mathrm{Fe_2O_3} \cdot z\mathrm{H_2O}$, *e.g.*:—

$$\mathrm{Fe(CH_3CO_2)_3 + 2H_2O = Fe(OH)_2(CH_3CO_2) + 2CH_3COOH.}$$

(Ferric phosphate is somewhat soluble in solutions of ferric chloride or acetate; hence only a slight excess of ferric chloride is added, and all the excess of iron is then precipitated as basic acetate.)

By the above process the phosphoric acid is entirely eliminated, and the calcium, barium, strontium and magnesium, which were originally present as phosphates, now remain in solution as soluble salts, which can be analysed in the usual way, *i.e.* by precipitation in their proper groups (V. and VI.).

Many of the changes involved in the operations here described can be more satisfactorily explained in terms of the ionisation hypothesis; the older views have been given however, for the sake of comparison. Thus the action of sodium acetate on hydrochloric acid may, as far as the essential change is concerned, be represented as

$$\mathrm{H^{\cdot} + CH_3CO_2{}' \rightleftarrows CH_3CO_2H,}$$

the sodium and chlorine ions taking practically no part. The concentration of the hydrogen ions (from the hydrochloric acid) is consequently greatly diminished, *i.e.* the solution becomes much less strongly acid; if excess of sodium acetate is employed the hydrogen ions are still further 'suppressed,' as explained on page 65.

'Insoluble' salts of weak acids dissolve in strong acids owing, as previously stated, to the tendency to form the less ionised weak acid* at the expense of the hydrogen ions of the strong acid. The concentration of the anions of the weak acid will therefore be smaller as that of the hydrogen ions is greater. The solubility in acids of the phosphates, oxalates, &c. with which we are here concerned, will depend on the degree of ionisation of the free acids, and on the solubilities of the particular salts in water—other things being supposed equal.

The phosphates of Fe, Cr, Al are less soluble in water than those of Ca, Ba, Sr, Mg, and a smaller concentration of the anions $\mathrm{PO_4{}'''}$ is therefore required in order that the solubility product of the former may be reached; the concentration of $\mathrm{H^{\cdot}}$ which remains after addition of sodium acetate is sufficient to reduce that of $\mathrm{PO_4{}'''}$ below the critical value in case of the latter, but is insufficient in case of the former. Similar explanations apply to the oxalates and fluorides.

* Or its more stable ions, *e.g.* $\mathrm{PO_4{}''' + H^{\cdot} \rightleftarrows HPO_4{}''}$.

ALTERNATIVE METHODS. Third Group.

For the detection of chromium and aluminium in this group, instead of fusion with Na_2CO_3, &c., the moist precipitate (or the nearly neutralised solution of the ppt. in HCl) may be boiled with sodium peroxide, the boiling being continued to decompose the excess of peroxide. This converts the Cr into chromate as before, and a portion of the same solution can also be tested for Al by just acidifying with HCl and adding NH_3. This procedure is perhaps easier than the fusion method, and it has the advantage that the commercial peroxide is free from Al. It has the disadvantage however of not indicating Mn. Potassium percarbonate, which is now obtainable as a commercial article, may be used in place of sodium peroxide.

The separation of phosphoric acid by ferric chloride in presence of sodium acetate and acetic acid is usually considered a troublesome process, and many attempts have been made to devise more simple methods, but it is questionable whether any of these can be considered advantageous. For example:—

Phosphates of Ca, Ba, Sr may be dissolved in the least possible quantity of HCl and the solution mixed with dilute H_2SO_4 and about $\frac{1}{3}$ of the total volume of alcohol. After standing for some hours the metals are obtained as sulphates, and the solution contains the phosphoric acid.

Oxalates of Ca, Sr, Ba may be treated similarly.

The phosphates of Ca, Ba, Sr, Mg may be dissolved in nitric acid and pure mercury added in such quantity that some remains undissolved. The mixture is evaporated to dryness on a water bath to completely expel excess of HNO_3, extracted with water and filtered. The residue contains all the PO_4 as mercury salt, and the Ca, &c. remain in solution (together with some Hg′ and Hg″ salt, which are removed in the usual way).

Metallic tin may be used instead of metallic mercury, the phosphates being dissolved in concentrated HNO_3, tin foil added, and the mixture evaporated to small bulk; it is then poured into water and allowed to stand for several hours, after which the metals will be left in solution free from PO_4.

TABLE IV. [Fourth Group.]

NiS, CoS, ZnS, MnS.

Wash; digest with cold dilute hydrochloric acid.

Filter

Residue (if not black, neglect)

Examine a portion with the borax bead *.

Blue bead in both flames indicates Co.

Brownish-violet in oxidising flame } Ni.
Grey in reducing flame (after a time) }

Dissolve remainder in the least possible quantity of HCl with a drop of HNO_3. (Filter off S if necessary.)

Nearly neutralise with NaHO. Add solution of (pure) KCN till the ppt. which is first formed is just redissolved. Boil for several minutes in an open dish. Filter off any slight ppt., and add a clear solution of HgO in $Hg(CN)_2$ †. Boil.

Filter

Ppt. (pale green)	Solution
NICKEL. Wash thoroughly and confirm by borax bead.	Evaporate to dryness and test residue for COBALT by borax bead §.

Solution ‡

Boil to expel H_2S. Cool, and add NaHO *in excess* without boiling.

Filter

Ppt.	Solution
Fuse with Na_2CO_3 (and a little KNO_3) on platinum foil. Blue-green mass. MANGANESE.	Pass H_2S. White (or nearly white) ppt. ZINC. (May be further confirmed by roasting ppt. on charcoal before the blowpipe and heating residue with cobalt nitrate. Green mass.)

* The borax bead test will almost certainly indicate cobalt even in presence of much nickel. In many cases, where more than mere traces are present, nickel may be detected as follows:—The neutralised solution is saturated with potassium chloride and potassium nitrite (solid or saturated solution) is added with some acetic acid; this will completely and rapidly precipitate cobalt (and traces of nickel), and nickel may then be detected in the filtrate by ammonium sulphide.

† Prepared by boiling freshly precipitated HgO in strong solution of $Hg(CN)_2$ and filtering. [NaClO, or bromine + NaHO, may be used instead, but solution must not then be boiled. The nickel will then be precipitated as black $Ni(OH)_3$.]

‡ Some IRON may also be present in this solution if much alkaline phosphate was originally present. Test a few drops therefore with potassium ferrocyanide.

§ Or add mercurous nitrate which precipitates $Hg_3Co(CN)_6$ (white). This on ignition leaves black Co_3O_4. Confirm by borax bead.

EXPLANATION OF TABLE IV.

Zinc and manganese sulphides dissolve readily in cold dilute hydrochloric acid (forming chlorides $ZnCl_2$ and $MnCl_2$, with evolution of H_2S); whilst nickel and cobalt sulphides are only dissolved in traces which do not interfere with the detection of zinc and manganese (see page 62).

The residue consisting of NiS and CoS is examined with the borax bead. If only nickel is indicated, it is not usually necessary to examine further, but if cobalt is found, the process of separation of nickel and cobalt must be gone through, since the blue given to the borax bead by cobalt may completely mask the nickel colour. It is safer however always to go through the entire process in either case, especially if small quantities have to be looked for.

For the purpose of separating nickel and cobalt a large number of different processes have been recommended; the old-established method given in the Table works well if sufficient care is taken.

The sulphides are dissolved in a small quantity of aqua regia and the excess of acid removed by evaporation, or by nearly neutralising with NaOH, and a solution of potassium cyanide is added drop by drop. The first addition of KCN causes the precipitation of the simple (ous) cyanides $Ni(CN)_2$ (green) and $Co(CN)_2$ (reddish-brown); on further addition these redissolve, forming (the ions of) the complex single salts $K_2[Ni(CN)_4]$ (yellow solution) and $K_4[Co(CN)_6]$ (brown solution). The latter salt is very easily oxidised by boiling the solution in the air (or addition of hypochlorites, &c.), giving the ions of another complex single salt (the change being analogous to the oxidation of a ferrocyanide to a ferricyanide),

$$\underset{\text{Pot. cobaltocyanide}}{2K_4Co(CN)_6} + H_2O + O = \underset{\text{Pot. cobalticyanide}}{2K_3Co(CN)_6} + 2KOH.$$

Potassium cobalticyanide gives a yellow solution and is remarkably stable; it shews none of the ordinary reactions of cobalt ions, and is not decomposed by hypochlorites, &c. or mercuric oxide. The nickel compound $K_2Ni(CN)_4$ however is comparatively unstable, tending to partially revert to the double salt $2KCN . NiCN_2$ [or $Ni(CN)_4'' \rightleftarrows Ni^{\cdot\cdot} + 4CN'$].

Addition of hypochlorites (or caustic soda + chlorine or bromine) causes the precipitation of black nickelic hydroxide $Ni(OH)_3$,

$$2Ni(CN)_2 + 4NaOH + NaClO + H_2O = 2Ni(OH)_3 + NaCl + 4NaCN,$$

or if freshly precipitated mercuric oxide is added the nickel is precipitated as $Ni(OH)_2 . Ni(CN)_2$. It is preferable to dissolve the mercuric oxide in mercuric cyanide so as to obtain a clear solution of the oxycyanide (probably $HgO . Hg(CN)_2$); this on heating with the solution of nickel salt precipitates green nickelous hydroxide,

$$Ni(CN)_2 + HgO + H_2O = Ni(OH)_2 + Hg(CN)_2.$$

EXPLANATION OF TABLE IV. (*continued*).

The cobalt remaining in solution as cobalticyanide may then be precipitated as mercurous cobalticyanide, and the latter decomposed by heat, or the solution may simply be evaporated to dryness; in either case the residue is tested by means of the borax bead. The evaporation method is sometimes inconvenient owing to the large amount of K or Na salts which have accumulated.

The manganese and zinc obtained in the solution after treating the sulphides with dilute HCl are now separated by addition of excess of caustic soda. Both are first precipitated as white hydroxides $Mn(OH)_2$ and $Zn(OH)_2$, but the latter readily dissolves in excess, forming sodium zincate Na_2ZnO_2 (*i.e.* the zinc hydroxide acts as an acid, giving $2H^{\cdot}$ and ZnO_2''). The latter salt is rather easily hydrolysed, hence $Zn(OH)_2$ is reprecipitated on diluting and boiling; strong cold NaOH is therefore used in the above process. The instability of the ZnO_2 ions is shewn by the fact that H_2S precipitates ZnS from the solution of sodium zincate,

$$Na_2ZnO_2 + 3H_2S = ZnS + 2NaHS + 2H_2O.$$

The manganous hydroxide which remains undissolved by excess of NaOH very rapidly turns brown on exposure to air owing to formation of intermediate oxides $xMnO \cdot yMnO_2 \cdot zH_2O$. Manganese is confirmed in this precipitate by fusion with sodium carbonate in excess in presence of air (or some other oxidising agent such as KNO_3),

$$Mn(OH)_2 + Na_2CO_3 + O = \underset{\text{blue green mass}}{Na_2MnO_4} + H_2O + CO_2.$$

ALTERNATIVE METHODS. Fourth Group.

Amongst other methods for separating the members of this group the following may be referred to:—

Manganese may be separated from zinc, nickel, or cobalt, by taking advantage of the fact that in acetic acid solution the three latter are completely precipitated by H_2S as sulphides, manganese remaining in solution (see page 68). The hydroxides are dissolved in a little HCl, sodium acetate added in excess, and H_2S is passed into the solution.

Nickel and cobalt may be separated—(or detected when present together)—

(*a*) By the potassium nitrite method. The concentrated solution of the chlorides is nearly neutralised and mixed with an excess of a strong solution of potassium nitrite and some acetic acid; a yellow crystalline precipitate of potassium cobaltinitrite is produced, nickel remaining in solution (from dilute solutions the precipitate separates only after standing in a warm place for several hours).

As in the case of the cyanide method, the cobalt here becomes oxidised, and (with the elements of nitrogen and oxygen) forms the complex anion $Co(NO_2)_6'''$. The resulting change may be regarded as taking place in the following stages:—Cobaltous nitrite is first formed by double decomposition and is then oxidised by nitrous acid to cobaltic nitrite $Co(NO_2)_3$, the nitrous acid being reduced to the state of nitric oxide; cobaltic nitrite then reacts with potassium nitrite to give potassium cobaltinitrite $K_3Co(NO_2)_6$. This method gives a very efficient separation. If excess of potassium chloride is added the precipitation of cobalt is said to be complete in about a minute (owing to the influence of the common ion) and nickel may be at once tested for in the filtrate. Some nickel however will be carried down in the precipitate when this modification is adopted.

(*b*) Solutions of cobaltous salts give a blue colour when mixed with a concentrated solution of ammonium sulphocyanate; this colour appears to be due to the complex single salt $(NH_4)_2[Co(CNS)_4]$, which is soluble in many organic solvents. This compound breaks down when the solution is diluted with water, the blue colour of the solution giving place to the pink colour due to $Co^{\cdot\cdot}$. If now the decolorised solution is shaken with a mixture of amyl alcohol and ether, the blue colour reappears in the upper layer. This reaction is very delicate for traces of cobalt in presence of nickel, the latter giving no colour. Ferric salts interfere with the test, since $Fe(CNS)_3$ (red) also dissolves and masks the blue colour, but this can be obviated by addition of a little Na_2CO_3 solution, which removes the iron.

(*c*) Potassium ferricyanide in presence of ammonium chloride precipitates both nickel and cobalt as ferricyanides; on digesting the precipitate with strong ammonia the nickel salt dissolves, leaving the cobalt salt. (On separation the latter has a tendency to run through the filter, but this difficulty may be removed by addition of a few drops of a solution of alum before precipitation.)

(*d*) Nitroso β naphthol $C_{10}H_6(NO)OH$ dissolved in acetic acid when added to a solution of the chlorides, containing free HCl, precipitates all the cobalt, leaving nickel in solution.

(*e*) The solution is boiled with an excess of barium carbonate, cooled, and bromine water is added in excess. This precipitates only the cobalt. Or the HCl solution to be tested may be saturated with chlorine and excess of barium carbonate added.

(*f*) Potassium persulphate in excess gives, on warming, a dark brown ppt. of $Co_3O_4 . 3H_2O$, leaving nickel in solution; this method of separation however appears to be imperfect.

(*g*) Dimethyl glyoxim $CH_3C(N.OH).C(N.OH).CH_3$ (for preparation see *Ber.* 1905, 2522) is said to be an extremely delicate test for nickel, with which it gives a scarlet red precipitate. Cobalt does not interfere unless present in large proportion; in the latter case excess of ammonia is added, which converts cobalt into the condition of complex ions.

TABLE V. [Fifth Group.]

$BaCO_3$, $SrCO_3$, $CaCO_3$.

Dissolve the main portion of the ppt. in the least possible quantity of *dilute* HCl*.

Test a part of the solution for Ba and Sr by adding $CaSO_4$ and warming.

$$\begin{cases}\text{Immediate ppt.} = \text{Ba,}\\ \text{ppt. after a time} = \text{Sr.}\end{cases}$$

If no ppt. even on standing, test remainder of solution at once for Ca as below†.

If Ba or Sr are present, evaporate remainder of solution to small bulk, add H_2SiF_6 in excess, and an equal volume of alcohol.

Filter

<table>
<tr><th>Ppt.</th><th>Solution</th></tr>
<tr><td>BARIUM.

Confirm by dissolving another portion of the $(NH_4)_2CO_3$ ppt. in acetic acid, and adding potassium chromate.

Yellow ppt. = Ba.

Dissolve ppt. in HCl and try flame-test.</td>
<td>To a portion add $CaSO_4$, heat, and allow to stand. White ppt. after a time STRONTIUM.

If Strontium is present, add dilute H_2SO_4 to remainder of solution, boil, and allow to stand some time.

Filter
<table>
<tr><th>Ppt.</th><th>Solution †</th></tr>
<tr><td>Neglect.</td><td>Add NH_3 till alkaline (filter if necessary), and ammonium oxalate. White ppt. insoluble in acetic acid.

CALCIUM.

Dissolve ppt. in HCl and try flame-test.</td></tr>
</table>
</td></tr>
</table>

* In most cases information can be obtained by trying the flame-test with a portion of this solution. Ba gives a green flame, Sr crimson, Ca orange-red.

EXPLANATION OF TABLE V.

On treating the precipitate of barium, strontium and calcium carbonates with hydrochloric acid, the metals are obtained as chlorides, carbon dioxide being evolved. Dilute acid must be employed for this purpose since barium chloride is precipitated by strong HCl (see page 66).

Calcium sulphate is sufficiently soluble in water for its solution to be used as a test for barium and strontium, whose sulphates are practically insoluble. [At ordinary temperatures the solubilities are approximately $CaSO_4\ 2H_2O$ 1 in 380, $SrSO_4$ 1 in 7000, $BaSO_4$ 1 in 344000.] The use of calcium sulphate for this initial test is preferable to that of dilute sulphuric acid or other soluble sulphates, since the latter may precipitate calcium as well if the solution is sufficiently concentrated. It is true that calcium sulphate itself might, from a nearly saturated solution, be precipitated by a very concentrated solution of a soluble calcium salt, but such conditions are not likely to be met with in the operations here described.

The special tests to be applied in detecting strontium and calcium would also give similar reactions with barium, hence the barium is first removed by taking advantage of the insolubility of $BaSiF_6$ in dilute HCl or of $BaCrO_4$ in acetic acid. For a similar reason strontium is removed before testing for calcium; this is done by adding dilute sulphuric acid which precipitates the strontium (practically) completely, but enough calcium sulphate will always remain in solution to be indicated by the delicate reaction with ammonium oxalate. Calcium oxalate is practically insoluble in water and in acetic acid, but dissolves in strong acids; hence the solution is made alkaline with ammonia before applying the test.

ALTERNATIVE METHODS. Fifth Group.

Barium may be separated from strontium and calcium by means of potassium chromate, which in *acetic acid* or *dilute neutral* solution precipitates only $BaCrO_4$.

Or the metals may be obtained as *chlorides* as before, the solution evaporated to dryness, and the residue digested with absolute *alcohol*. $SrCl_2$ and $CaCl_2$ dissolve, but $BaCl_2$ remains insoluble.

Strontium may be separated from calcium by converting the metals into *sulphates* and digesting these with a strong hot solution of *ammonium sulphate*. $CaSO_4$ dissolves, $SrSO_4$ remains insoluble. The calcium here forms with the SO_4 a complex anion, the resulting salt being represented by the formula $(NH_4)_2[Ca(SO_4)_2]$.

Or the metals may be obtained as *nitrates*, the solution evaporated to dryness (care being taken that the temperature is not high enough to decompose the latter), and the residue digested with absolute *alcohol*. $Ca(NO_3)_2$ dissolves and $Sr(NO_3)_2$ remains insoluble.

Barium and strontium may be separated from calcium by converting the metals into *nitrates*, evaporating to dryness as before, and adding a small quantity (1 or 2 c.c.) of concentrated *nitric acid*. $Ba(NO_3)_2$ and $Sr(NO_3)_2$ remain insoluble, $Ca(NO_3)_2$ dissolves.

TABLE VI.

Solution may contain Mg, K, Na, NH_4.

Evaporate to dryness. Heat residue to low redness until fumes cease to be evolved.

1. Dissolve a portion of residue in water (and a drop of dil. HCl if necessary). Test the solution with NH_4Cl, NH_3 and sodium phosphate. Warm, shake, and allow to stand. White ppt. (crystalline from dilute solutions or on standing) = MAGNESIUM*.

2. Dissolve the remainder in the least possible quantity of water†. Filter if necessary. Test a portion of the solution by stirring on a watch glass with 'platinic chloride'‡. Yellow ppt. in lines = POTASSIUM§.

   Examine another portion by the flame-test on a *clean* platinum wire. Strong and persistent yellow coloration = SODIUM‖. Violet coloration POTASSIUM.

Test a portion of the *original* substance or solution for ammonium by boiling with soda. Fumes of ammonia (recognised by odour and action on red litmus paper) AMMONIUM.

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* A slight flocculent ppt. which does not become crystalline on standing may be due to Ba, Ca, Al, &c. In doubtful cases, therefore, add a mixture of ammonium sulphate, ammonium oxalate and ammonia, boil and filter before testing for Mg.

† If much Mg is indicated it should be removed before testing for K and Na. This may be done by adding $Ba(OH)_2$, filtering, removing the excess of Ba salt with ammonium carbonate, evaporating, and igniting to remove ammonium salts.

‡ More correctly hydrochloroplatinic acid H_2PtCl_6.

§ If iodides are present, H_2PtCl_6 will produce a strong red or brown colour.

$$H_2PtCl_6 + 2KI = H_2PtCl_4 + 2KCl + I_2.$$

In this case it is advisable to evaporate with HCl to remove HI before testing.

‖ Viewed through blue glass, the sodium light is cut off so that the potassium colour becomes visible; a comparison should however be made with the known substances since without experience the tints are misleading. Confirm sodium, if possible, by dihydroxytartaric acid.

EXPLANATION OF TABLE VI.

Before testing for the remaining metals (Mg, K, Na) it is necessary to remove th ammonium salts which have accumulated in the solution during the previous operation since ammonium gives reactions similar to those of potassium with platinic chloride, tartari acid or sodium cobalti-nitrite. The precipitation of $Mg(OH)_2$ by $Ba(OH)_2$ is moreove entirely prevented, and that of $Mg(NH_4)PO_4$ by sodium phosphate is less complete, if exces of ammonium salts are present. The solution is therefore evaporated to dryness and th residue gently ignited as long as fumes are evolved; too high a temperature has to b avoided, otherwise the chlorides of K and Na may partially vaporise.

A portion of the residue is dissolved in water (and a drop of HCl if necessary, sinc $MgCl_2$ may leave a sparingly soluble oxychloride on evaporation of its aqueous solution and tested for magnesium by means of sodium phosphate in presence of ammonium chlorid and ammonia

$$Na_2HPO_4 + MgCl_2 + NH_3 = Mg(NH_4)PO_4 + 2NaCl.$$

[The ammonium chloride is here added to prevent the precipitation of $Mg(OH)_2$ by th ammonia; its action has been explained on page 69.]

The remainder of the residue is dissolved in water (filtered if necessary) and examine for potassium and sodium. If much magnesium has been indicated it is advisable to remov it before testing for potassium and sodium; this may be done by precipitating as Mg(OH) by means of barium hydroxide, the excess of barium being afterwards removed by ammoniun carbonate and the ammonium by heat as above. Mercuric oxide may be used instead o $Ba(OH)_2$ and the mercury removed by heating to low redness. Or a solution of the chloride may be evaporated to dryness with ammonium oxalate and the residue heated; this convert the metals into carbonates and on extraction with water $MgCO_3$ remains insoluble.

Potassium is detected by means of so-called 'platinic chloride' solution. This solutio (which is prepared by dissolving platinum in aqua regia) contains the platinum togethe with the chlorine as a complex anion $PtCl_6''$; it is to be regarded therefore as *hydrochloro platinic acid* $H_2(PtCl_6)$. With potassium salts this gives the yellow crystalline precipitat of the corresponding complex single salt $K_2(PtCl_6)$. The latter is very sparingly solubl in cold water, even in presence of HCl, and is practically insoluble in alcohol. (Sodiun forms a similar salt, $Na_2PtCl_6 . 6H_2O$, which is easily soluble in water and in alcohol.)

Potassium may also be detected by *tartaric acid* provided strong acids are absent. Th crystalline acid potassium tartrate, $KHC_4H_4O_6$, is sparingly soluble in water, but dissolve in strong acids. It is very sparingly soluble in acetic acid—less so if sodium acetate i added.

Perchloric acid is also employed as a test for potassium since $KClO_4$ is sparingly solubl in water, even if HCl is present. [H_2PtCl_6 and $HClO_4$ are fairly strong acids, $H_2C_4H_4O$ is a weak acid; the $H^{\cdot}$ in a solution of hydrochloric acid has therefore little solvent

action on salts of the first two, but it is sufficient to cause the dissolution of $KHC_4H_4O_6$ (forming little ionised $H_2C_4H_4O_6$) see pages 65 and 83.]

Other tests for potassium are *sodium cobalti-nitrite* $Na_3[Co(NO_2)_6]$ which in acetic acid solution precipitates yellow crystalline $K_2Na[Co(NO_2)_6]$, and sodium bismuth-thiosulphate $Na_3[Bi(S_2O_3)_3]$ which in aqueous alcoholic solution precipitates the corresponding potassium salt (yellow).

Sodium is usually detected only by the flame-test. Since however traces of sodium are almost universally present as impurity it is advisable to obtain some idea of the quantity present. Some propose to remove the potassium, if present, as K_2PtCl_6, evaporate the filtrate decompose the Na_2PtCl_6 by heating, and extract the residual NaCl from Pt by water. There are precipitation tests, however, which will directly indicate sodium, even though potassium is present.

(*a*) *Dihydroxytartaric acid* is added to a neutral solution of a sodium salt and the mixture just neutralised with a drop or two of ammonia or dilute potassium carbonate. If sodium is present a white crystalline precipitate is obtained, on stirring, of sodium dihydroxytartrate $Na_2C_4H_4O_8 . 3H_2O$. [This reaction is very delicate if the solutions are kept cold, the solubility of the sodium salt at 0° being about 1 in 2500.]

(*b*) *Acid potassium pyroantimonate* $K_2H_2Sb_2O_7$* gives in neutral solutions a white crystalline precipitate of $Na_2H_2Sb_2O_7 . 6H_2O$ (solubility about 1 in 350). Free alkalis retard its formation, and acids decompose it.

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* Formerly called acid potassium metantimonate.

DETECTION OF MORE THAN ONE ACID RADICLE.

Preliminary examination (by treatment with HCl and H_2SO_4) as in the case of one metal, page 56*.
Make solution, and remove metals if necessary, as directed on page 59.
Divide solution into several parts, and test as follows:—

1. Acidify with dilute HCl and add Barium Chloride.

White ppt. indicates:
- SULPHATE. Confirm by strontium nitrate in another portion of solution.
- SILICOFLUORIDE. Confirm by heating this ppt. (or original solid) with concentrated H_2SO_4 in platinum vessel.

2. Add ammonia till alkaline (filter off any ppt.†) and Calcium Chloride.

White ppt. indicates *Oxalate, Fluoride, Phosphate, Arsenate, Borate, Tartrate, Citrate, Sulphate* (from strong solutions only). (Carbonate and silicate if not previously removed during neutralisation, &c. of original solution.)

Filter‡, wash ppt. and digest it with acetic acid.

FILTER

RESIDUE. *Oxalate, Fluoride.* (*Sulphate*)	SOLUTION
Wash, dry and heat to low redness; treat with acetic acid. Effervescence indicates OXALATE. Examine residue for FLUORIDE by H_2SO_4 test.	Add $FeCl_3$ drop by drop. Yellowish-white ppt. indicates {Phosphate, Arsenate} Dissolve ppt. in dilute HCl. Add SO_2 and boil until excess of SO_2 is expelled. Pass H_2S. Yellow ppt. indicates ARSENATE. If this is present remove it all by H_2S. Boil off excess of H_2S and confirm PHOSPHATE by ammonium molybdate§.

3. Add silver nitrate *in excess* and dilute HNO_3.

FILTER

Ppt. indicates *Chloride* (white), *Cyanide* (white), *Sulphocyanate* (white), *Ferricyanide* (orange) — easily soluble in ammonia Bromide (yellowish-white) . . . . sparingly soluble Iodide (yellow), Ferrocyanide (white), (Sulphide) (black) . . . . . . nearly insoluble To get an idea of the quantity dissolved shake up with excess of ammonia, filter and acidify filtrate with dilute HNO_3.	To solution add ammonia drop by drop, and carefully observe colour of any ppt. formed at the neutral zone, where the liquids meet, Phosphate, (Arsenite) — yellow. Arsenate, brick-red (Chromate, crimson-red) Oxalate, tartrate, borate and some others, white.

4. Acidify with dilute HCl and add $FeCl_3$ until no further change.
Dark blue ppt. indicates FERROCYANIDE. Blood-red colour bleached by $HgCl_2$, SULPHOCYANATE.
Filter‖ if necessary and add $FeSO_4$: Dark blue ppt. indicates FERRICYANIDE.

5. Test specially for *Borate* in original solution by the H_2SO_4 and alcohol test. Also for *Acetate* (*Chromate, Manganate, Permanganate*), *Nitrate* ¶, *Chlorate* as in detecting one acid radicle, or as mentioned in further separations.

* Note however that when more than one acid is present the results of the preliminary examination may be modified or obscured.
† See footnote † on page 61.
‡ A precipitate on boiling the filtrate probably indicates *citrate*.
§ If much HCl is present it should be first removed by evaporation with HNO_3.
‖ If the blue compound remains in solution add excess of strong KCl solution before filtering.
¶ The $FeSO_4$ test for nitrates is not suitable if iodides or bromides are present; in such cases either remove the halogen acids by silver sulphate or employ reduction tests for nitrate (see pages 41 and 97).

REMARKS ON THE DETECTION OF MORE THAN ONE ACID RADICLE.

Experience shews that it is not advisable to attempt a scheme for the complete separation of the acid radicles analogous to that used in the case of metals. In the first place the acid radicles are, with few exceptions, compounds instead of single elements and may often undergo changes during the process of analysis; thus sulphites easily become oxidised to sulphates, hypochlorites are easily reduced to chlorides, and so on. Again, some of the salts or free acids cannot co-exist in solution; hypochlorite and sulphite for example yield chloride and sulphate; free iodic and hydriodic acids give iodine and water; when hydrosulphuric and sulphurous acids come together sulphur is precipitated and pentathionic acid, &c. formed.

It is best therefore in most cases to work by a process of exclusion and then to apply special methods of separation to those groups of acids which may have been indicated. By carefully noting the results obtained in the Preliminary Examination and those given by the tests mentioned on page 95, it will generally be easy to decide which acids are excluded and which groups must be further examined.

A few of the more commonly occurring special separations are given below.

Iodide and *Iodate.*

If pure, neither of these salts alone gives any free iodine when treated with *dilute* sulphuric, hydrochloric or acetic acid in the cold. But if both are present, the free acids liberated on acidification at once decompose one another with liberation of iodine

$$5HI + HIO_3 = 3I_2 + 3H_2O.$$

Test a portion of the original solution therefore for *iodide* by chlorine water and CS_2 and another portion by acidifying as above, and again testing for iodine by CS_2. The liberation of iodine in the latter case confirms *iodate*, provided no other oxidising agent is present.

Nitrate in presence of other acid radicles.

The ordinary test for nitrate by means of ferrous sulphate and strong sulphuric acid is obviously unsuitable in presence of nitrites, iodides, bromides, chlorates, hypochlorites or tartrates, since in such cases the formation of the brown ring is either prevented or obscured. It becomes necessary therefore either to remove or destroy the acid radicles mentioned before testing for nitrate, or else to employ other tests for the latter, such as the reduction to nitrite or to ammonia. See page 41.

Nitrate and *Chlorate.*

The tests previously described for these two acid radicles singly would be partially or entirely obscured if both are present; hence special methods are necessary.

I. Boil the mixture with caustic soda; if ammonia is given off, from ammonium salts (amides, &c.), boil until no more ammonia can be detected. Add zinc dust and again boil; if ammonia is now given off it indicates *Nitrate* (or Nitrite),

$$NaNO_3 + 7NaOH + 4Zn = 4Zn(ONa)_2 + 2H_2O + NH_3.$$

Chlorate will at the same time be reduced to *Chloride*; test solution for this by adding HNO_3 in excess and $AgNO_3$.

If a *chloride* is *originally* present as well as Chlorate and Nitrate, it must first be eliminated by means of silver sulphate, any excess of the latter being removed by caustic soda.

II. A simpler but perhaps less accurate method is to heat the solid mixture to low redness; chlorate becomes chloride and nitrate becomes nitrite. Test one portion for chloride as above, and the other for nitrite by means of (1) ferrous sulphate, (2) KI and dilute H_2SO_4 and (3) potassium permanganate, (4) aniline sulphate.

Nitrate and *Nitrite.*

There are many tests which distinguish nitrite, even though a nitrate is present; but the converse problem—the identification of nitrate in presence of nitrite—necessitates the previous removal of nitrite, except in the case of the brucine test when carefully applied under certain conditions, see page 42.

Test a portion of the mixture for Nitrite as above. If present destroy it entirely by warming with urea in excess and dilute H_2SO_4,

$$CO(NH_2)_2 + 2HNO_2 = 3H_2O + CO_2 + 2N_2,$$

and test remaining solution for nitrate by $FeSO_4$ and concentrated H_2SO_4 (or by reducing to nitrite with zinc, &c.).

The nitrous acid may also be destroyed by means of ammonium chloride, or by action of hydriodic acid in an atmosphere of carbon dioxide.

In all these methods there is danger of small quantities of nitric acid resulting from decomposition of nitrous acid. A safer method consists in destroying the nitrous acid by means of hydrazine in the cold. The concentrated solution to be examined is slowly dropped on to finely powdered hydrazine sulphate; when the change is completed the resulting solution is tested for nitrate, preferably by the nitron test*.

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* This test, which has been recently discovered by Busch (*Ber.* 1905, 861) depends on the very sparing solubility of the nitrate of a new base, which is now sold under the name of 'Nitron' (Diphenylendo-anilodihydrotriazole $C_{20}H_{16}N_4$). The base when dissolved in dilute acetic acid gives a colourless crystalline precipitate even in extremely dilute solutions of nitrates (about 1 in 60000).

Chloride, Bromide and *Iodide.*

I. To a neutral solution add $CuSO_4$ in slight excess and sulphurous acid; this precipitates the iodide as cuprous salt,

$$2KI + 2CuSO_4 + H_2SO_3 + H_2O = 2CuI + 2KHSO_4 + H_2SO_4.$$

Filter. Wash ppt. and confirm iodide by heating it with concentrated H_2SO_4. Remove excess of copper from the filtrate by boiling with NaOH in just sufficient excess. Evaporate solution to dryness and mix residue with dry $K_2Cr_2O_7$ and concentrated H_2SO_4. Distil (in small retort or distilling-flask). Bromides give rise to free bromine, and chlorides to chromyl dichloride, both of which form deep red vapours easily condensed to liquid,

$$6KBr + K_2Cr_2O_7 + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Br_2,$$
$$4KCl + K_2Cr_2O_7 + 3H_2SO_4 = 3K_2SO_4 + 2CrO_2Cl_2 + 3H_2O.$$

Collect the resulting vapours in water. Bromine dissolves unchanged and CrO_2Cl_2 is decomposed giving hydrochloric and chromic (or bichromic) acids, see page 14,

$$CrO_2Cl_2 + H_2O = H_2CrO_4 + 2HCl.$$

Confirm *bromine* by shaking up with CS_2 and chromate (and consequently *chloride*) by means of H_2O_2 and ether, or by lead acetate.

II. To a *dilute* solution of the mixture, in the cold, add sodium acetate and ammonium persulphate; under these conditions only *iodine* is liberated; allow to stand until the change is complete and remove the liberated iodine by repeated shaking with CS_2. Now warm the mixture to about 80°, adding more persulphate if necessary and a little dilute sulphuric acid; *bromine* is then evolved and may be removed by passing a current of air through the heated solution. Test remaining solution for *chloride* by $AgNO_3$ and HNO_3.

Or the mixture may be at once heated with persulphate and a current of air passed, in this case the bromine and most of the iodine are removed; some of the iodine remains as iodate, but this does not interfere with the test for chloride if excess of HNO_3 is added.

Another method consists in boiling an acetic acid solution of the mixture with lead dioxide; this expels bromine and part of the iodine, the rest forming insoluble lead iodate; the chloride is not decomposed and can be detected in the filtrate as usual.

Under suitable conditions, iodine may be completely expelled by distillation with hydrogen dioxide in acetic acid solution, chloride and bromide remaining. Or iodine may be expelled by distillation with ferric sulphate and bromine with potassium permanganate, chloride remaining.

Chloride, Chlorate and *Perchlorate.*

Test one portion of the solution for chloride by silver nitrate and another portion for chlorate by the sulphurous acid and indigo test. To the remainder of the solution add sulphurous acid in excess and boil in order to reduce chlorate to chloride. Boil off excess of SO_2 and precipitate the chloride with silver sulphate, afterwards removing the excess of the silver by addition of sodium carbonate. Evaporate resulting solution to dryness and heat to redness to convert perchlorate to chloride. (Addition of (pure) lime renders the latter decomposition easier.) Extract with water, add nitric acid and test for chloride as above.

Or the perchlorate may be readily reduced to chloride by gentle fusion with sodium or potassium nitrite,

$$KClO_4 + 4KNO_2 = KCl + 4KNO_3.$$

Cyanide and *Cyanate.*

I. Test a portion for cyanide by means of ferrous salt, ferric salt and dilute H_2SO_4. To the remainder add dilute H_2SO_4 till just acid and heat gently until the vapours are free from HCN (this is ascertained by exposing a drop of NaOH, on filter paper to the fumes, and applying the Prussian blue test as above). The cyanate is in this way decomposed, giving rise to carbon dioxide and ammonium salt,

$$HCNO + H_2O = CO_2 + NH_3;$$

the ammonium is then confirmed by boiling the solution with excess of NaOH, or in case of small quantities by Nessler's test.

II. The cyanide may be removed by passing carbon dioxide into the solution until no more HCN can be detected (this may take an hour or more), and testing the remainder for cyanate by the cobalt acetate reaction (see page 39).

Cyanide, Ferrocyanide and *Ferricyanide.*

The cyanide may be removed as above with carbon dioxide or else by boiling the solution with magnesium chloride. Cyanide is tested for in the evolved gases and ferro- and ferri-cyanides are identified in the solution by means of iron salts. Ferricyanide in presence of ferrocyanide may also be further confirmed by warming with KI and dilute HCl, when iodine will be liberated:—

$$2H_3FeC_6N_6 + 2HI = 2H_4FeC_6N_6 + I_2.$$

Cyanide, Cyanate, Sulphocyanate and *Sulphide.*

Into a distilling flask provided with a stop-cock funnel, introduce a solution of cadmium sulphate and potassium-hydrogen-sulphate and boil until the air is expelled, the end of the exit tube dipping under a solution of caustic soda. Now run in the solution to be tested, slowly so that the vapours are absorbed. The sulphide is retained as yellow cadmium salt; the cyanate yield ammonium sulphate, as above; the cyanide yields HCN, which is absorbed and identified in the soda solution, and the sulphocyanate remains unaffected, and can be identified by means of $FeCl_3$.

Sulphite and *Carbonate.*

If much sulphite is present the SO_2 given off on acidification may mask the detection of carbon dioxide by the usual lime-water test; hence pass the gases through a small wash-bottle containing potassium bichromate and dilute H_2SO_4; the solution will be turned green, indicating the presence of *sulphite* (confirm by the zinc test) and the remaining gas can be tested for carbon dioxide as usual.

Sulphate, Sulphite, Thiosulphate and *Sulphide.*

Shake up solution with cadmium carbonate in excess and filter.

<table>
<tr><td rowspan="3">RESIDUE (CdS and excess of $CdCO_3$)
Wash, dissolve out excess of $CdCO_3$ with acetic acid and confirm *sulphide* in the yellow residue by heating with HCl and testing evolved gas for H_2S.</td><td colspan="3">SOLUTION
Add $BaCl_2$ in slight excess and filter.</td></tr>
<tr><td colspan="2">Ppt. = ($BaSO_4$ and $BaSO_3$). Wash. Digest with dilute HCl. Filter</td><td rowspan="2">SOLUTION
Heat with HCl. Yellow ppt. of sulphur and evolution of SO_2 indicates *Thiosulphate.*</td></tr>
<tr><td>RESIDUE
Barium *sulphate.*</td><td>SOLUTION
Add chlorine or bromine water. White ppt. of $BaSO_4$ indicates *Sulphite.*</td></tr>
</table>

Instead of $BaCl_2$, $Sr(NO_3)_2$ may be used and is perhaps preferable, since a strong solution of thiosulphate may be precipitated by the barium salt; the complete precipitation of the sulphate and sulphite takes much longer in this case.

Tartrate and Citrate.

To a concentrated solution add an excess of potassium acetate dissolved in alcohol, and, if necessary, a few drops of acetic acid. Add an equal bulk of alcohol, shake, stir, and allow to stand for some hours. Filter.

Crystalline ppt. often adhering to sides of vessel indicates *Tartrate.* Wash ppt. with a little water, dissolve in least possible NaOH, and confirm tartrate by mirror test and by H_2O_2 and Fe''.	SOLUTION Confirm citrate by neutralising and adding barium acetate, or add $CaCl_2$ to neutral solution and boil.

PROPERTIES AND REACTIONS OF SOME OF THE COMMONER OR MORE TYPICAL ORGANIC COMPOUNDS.

METHANE.

Marsh gas. CH_4. [Class. *Saturated hydrocarbon. Paraffin series.*]

Colourless gas. Sp. gr. 0·559 (air = 1). Nearly insoluble in water. Slightly soluble in alcohol. (At 20° one volume of water absorbs about 0·03 volumes and one volume of alcohol about 0·5 volumes.)

Burns in air; if pure the flame is only slightly luminous. Forms an explosive mixture with air or oxygen,

$$\underset{2\text{ vols.}}{CH_4} + \underset{4\text{ vols.}}{2O_2} = CO_2 + 2H_2O.$$

Reacts with chlorine or bromine only by substitution.

ETHANE.

C_2H_6. [*Class as above.*]

Colourless gas. Sp. gr. 1·036. Rather more soluble in water and alcohol than methane; in its other properties it is very similar. On explosion with oxygen,

$$\underset{4\text{ vols.}}{2C_2H_6} + \underset{14\text{ vols.}}{7O_2} = 4CO_2 + 6H_2O.$$

Examples of other members of the series of Paraffins (C_nH_{2n+2}) are found in 'Petroleum ether,' Gasoline, Ligroin, &c. which are mixtures of liquid paraffins (principally pentane, hexane, heptane, octane, &c.); vaseline (semi-solid) and paraffin wax (solid). The latter contain still higher members of the series.

The above hydrocarbons react with chlorine or bromine only by *substitution*. They are unacted upon by alkalis and, at ordinary temperatures, are practically unaffected by fuming nitric or sulphuric acids or by oxidising agents.

ETHYLENE.

Ethene. Olefiant gas. C_2H_4. [Class. *Unsaturated hydrocarbon. Olefine series.*]

Colourless gas. Sp. gr. 0·978. Slightly sweetish odour. Very slightly soluble in water. (At 20° one volume of water absorbs about 0·15 volumes, and one volume of alcohol about 2·7 volumes.)

Burns in air with luminous flame.

Forms an explosive mixture with air or oxygen:

$$\underset{2\text{ vols.}}{C_2H_4} + \underset{6\text{ vols.}}{3O_2} = 2CO_2 + 2H_2O.$$

Unites *directly* with chlorine or bromine, forming addition compounds $C_2H_4Cl_2$ (Dutch liquid) and $C_2H_4Br_2$. May also be absorbed slowly by fuming sulphuric acid (forming $C_2H_5HSO_4$) and by fuming nitric acid, being then oxidised to oxalic acid.

Mixed with twice its volume of chlorine and ignited, hydrochloric acid is formed and carbon separates as a dense black smoke,

$$C_2H_4 + 2Cl_2 = 4HCl + 2C.$$

ACETYLENE.

Ethine. C_2H_2. [Class. *Unsaturated hydrocarbon. Acetylene series.*]

Colourless gas. Sp. gr. 0·90. Characteristic disagreeable odour (perhaps due to impurity).

One volume of water at ordinary temperatures dissolves about 1·1 volumes, and one volume of alcohol about 6 volumes. It dissolves also in acetone.

Burns with very luminous, smoky flame. Combines directly with chlorine, forming $C_2H_2Cl_2$ and $C_2H_2Cl_4$; similarly with bromine.

A mixture of chlorine and acetylene sometimes explodes, giving hydrochloric acid with separation of carbon. It is absorbed by strong sulphuric acid.

Absorbed also by an ammoniacal solution of cuprous chloride, forming a brownish-red amorphous precipitate of cuprous acetylide $C_2Cu_2 . H_2O$, which is explosive when dry. With ammoniacal silver nitrate it gives a white or yellowish precipitate of the corresponding silver compound, which is also explosive. The formation of such metallic derivatives is often characteristic of the 'triple bond' $\cdot C \equiv C \cdot$

CHLOROFORM.

Trichloromethane. $CHCl_3$.

Colourless liquid. Characteristic odour; sweet, burning taste. B. P. 61·2. Sp. gr. 1·50 at 15°. Very slightly soluble in water; miscible in all proportions with alcohol, ether or benzene.

Heated with an alcoholic solution of caustic potash it yields potassium formate and potassium chloride,

$$CHCl_3 + 4KOH = H.COOK + 3KCl + 2H_2O.$$

Warmed with alcoholic solution of caustic potash and a drop or two of aniline it gives rise to phenyl isonitrile (also called phenyl isocyanide, carbylamine, or carbamine),

$$CHCl_3 + C_6H_5NH_2 + 3KOH = C_6H_5NC + 3KCl + 3H_2O.$$

This product has a characteristic and highly disagreeable odour; it is *poisonous*, and the above test must never be carried out in the open laboratory.

When heated with Fehling's solution the latter is rapidly reduced, red cuprous oxide being precipitated,

$$CHCl_3 + 5KOH + 2CuO = Cu_2O + K_2CO_3 + 3KCl + 3H_2O.$$

When mixed with a solution of α or β naphthol in strong caustic soda solution and heated to about 50° a blue colour is produced which afterwards changes to green and brown. (This reaction is also given by chloral and chloral hydrate.)

IODOFORM.

Triiodomethane. CHI_3

Pale yellow lustrous crystalline solid (hexagonal plates). Characteristic odour. M. P. 119°. Sp. gr. 2. When gently heated it sublimes unchanged; strongly heated it yields vapours of iodine. Iodine is also liberated when solutions of iodoform are exposed to air and sunlight. Nearly insoluble in water; more easily soluble in hot alcohol; easily soluble in ether, chloroform or carbon disulphide.

When made into a paste with moist finely divided silver, it yields acetylene.

METHYL ALCOHOL.

Wood Spirit. CH_3OH. [*Monohydric primary alcohol.*]

Colourless, volatile liquid; burns with pale blue flame. B. P. 66°. Sp. gr. 0·796 at 20°.

By gentle oxidation (*e.g.* by air in contact with heated platinum or copper) it yields formaldehyde :—

$$H.CH_2OH + O = H.CHO + H_2O.$$

By dipping a red hot coil of copper wire into the liquid, and repeating the operation a few times, the production of formaldehyde is easily recognised by the characteristic odour and by some of the tests mentioned on page 109 (*e.g.* by the resorcinol test).

By further oxidation, *e.g.* with potassium bichromate and sulphuric acid in the cold, it produces formic acid $H.COOH$, which may be distilled off and tested as on page 118. (Acetone and some other substances also yield formic acid by this treatment.)

Heated with a salicylate or a formate and strong sulphuric acid it yields methyl salicylate (oil of winter green) or methyl formate; these esters have odours which are somewhat characteristic, but which do not greatly differ from those of the corresponding ethyl esters,

$$C_6H_4(OH).COOH + CH_3OH = C_6H_4(OH).COOCH_3 + H_2O$$

$$H.COOH + CH_3OH = H.COOCH_3 + H_2O.$$

Pure methyl alcohol does not give the iodoform reaction (see ethyl alcohol) but the commercial article always contains acetone, and this does give the reaction.

ETHYL ALCOHOL.

Alcohol. Spirits of Wine. $C_2H_5.OH$. [*Monohydric primary alcohol.*]

Colourless volatile liquid; burns with pale blue flame. B. P. 78°. Sp. gr. 0·795 at 15°.

By oxidation with potassium bichromate and sulphuric acid it yields acetaldehyde :—

$$CH_3.CH_2OH + O = CH_3.CHO + H_2O.$$

Attention has to be paid to proportions and conditions; *e.g.* mix 1 part of the alcohol with about half its volume of strong sulphuric acid, cool and pour slowly on to a mixture of powdered potassium bichromate (about 1 part) and water (4 or 5 parts). The acetaldehyde may be distilled off (together with other products) and recognised by the tests on page 110.

By further oxidation (*e.g.* by potassium permanganate) acetic acid is produced.

Heated with (solid) sodium acetate and strong sulphuric acid it gives rise to ethyl acetate,

$$CH_3.COOH + C_2H_5OH = CH_3.COOC_2H_5 + H_2O.$$

Ethyl Alcohol (*continued*).

When a fairly dilute aqueous solution is mixed with a little iodine and caustic soda is then added, drop by drop, until the colour of the iodine disappears, the mixture on warming yields crystals of iodoform CHI_3. In very dilute solutions the separation may not occur for some time. The crystals are pale yellow (sometimes almost white when first separated) and consist of hexagonal plates or six-rayed stars; the odour is characteristic. The crystalline form is best observed by washing the precipitate and recrystallising from hot dilute alcohol.

This reaction is also given by acetone, acetaldehyde and by many other substances which contain such groups as ($CH_3.CO.C$) or ($CH_3.CHOH.C$).

For the identification of ethyl alcohol in small quantities, *p* nitrobenzoyl chloride may be used. This yields the ethyl ester of *p*· nitrobenzoic acid, which when recrystallised from petroleum and then from methyl alcohol melts at 57° (Buchner and Meisenheimer).

Or 3·5· dinitrobenzoyl chloride may be similarly employed. The resulting ethyl ester when washed with cold methyl alcohol and recrystallised from the same solvent, melts at 92—93° (Mulliken).

AMYL ALCOHOLS.

$C_5H_{11}.OH.$

Of these there are eight structurally isomeric modifications; the *ordinary commercial amyl alcohol* (which is the principal constituent of 'fusel oil') is a mixture of about 87 per cent. of isobutyl carbinol $CH(CH_3)_2.CH_2.CH_2OH$ with optically active secondary butyl carbinol $(C_2H_5)(CH_3)CH.CH_2OH$ and perhaps some normal amyl alcohol $CH_3.CH_2.CH_2.CH_2.CH_2OH$. It boils at about 129—132°, and has a somewhat disagreeable odour; the vapours which it gives off on heating produce coughing. Sp. gr. about 0·814 at ordinary temperatures. Soluble in about 39 parts of water at 15°. Miscible in all proportions with ethyl alcohol, chloroform, ether, benzene, &c.

Heated with sodium acetate and strong sulphuric acid it gives the agreeable and somewhat characteristic odour of Jargonelle pears, due to amyl acetate $CH_3.COO(C_5H_{11})$.

When oxidised with potassium bichromate and sulphuric acid it gives first an agreeable fruity odour of valeric aldehyde (or of amyl valerate) followed by the disagreeable odour of isovaleric acid.

Warmed with a little strong sulphuric acid it gives a red colour.

ETHYLENE GLYCOL.

Glycol. $\begin{matrix} CH_2OH \\ \dot{C}H_2OH \end{matrix}$. [*Dihydric alcohol.*]

Syrupy colourless liquid. B. P. 197·5°. Miscible in all proportions with water or alcohol; sparingly soluble in ether. Sweet taste.

Shaken with benzoyl chloride and aqueous caustic soda solution (Schotten-Baumann reaction) it yields a dibenzoate $C_2H_4(C_6H_5CO_2)_2$, which when washed and recrystallised from alcohol melts at 70—71°.

Nitric acid oxidises it to glycollic acid $CH_2OH.COOH$, and further, to oxalic acid.

When mixed, in aqueous solution, with ferrous sulphate and oxidised with rather less than the calculated quantity of hydrogen dioxide, it yields glycollic aldehyde $CH_2OH.CHO$. The latter can be recognised by gently warming with phenylhydrazine acetate which gives, after a time, a yellowish-brown crystalline precipitate of glyoxal dihydrazone $\begin{matrix} CHN_2H(C_6H_5) \\ \dot{C}HN_2H(C_6H_5) \end{matrix}$. The latter, after washing with a little cold alcohol and recrystallising from hot absolute alcohol, melts at 169—170°.

GLYCEROL.

Glycerine. $C_3H_5(OH)_3$ or $CH_2OH.CHOH.CH_2OH$. [*Trihydric alcohol.*]

If pure, a colourless crystalline substance melting at 17°. As ordinarily obtained it is a thick syrupy liquid having a sweet taste. Sp. gr. 1·265 at 15°. The pure substance boils at 290°; if small quantities of impurity (salts, &c.) are present it undergoes partial decomposition when boiled, but it may be distilled unchanged in steam.

Miscible in all proportions with water or alcohol; practically insoluble in ether or chloroform, but soluble in a mixture of ether and alcohol, or in acetone.

Heated with potassium hydrogen sulphate (some other dehydrating agents behave similarly, *e.g.* P_2O_5 or H_2SO_4) it yields acrolein or acrylic aldehyde,

$$C_3H_5(OH)_3 - 2H_2O = C_2H_3.CHO.$$

The vapours of acrolein will be recognised by their disagreeable odour and irritating effect on the eyes.

Like other alcohols, it undergoes esterification with acids (in presence of dehydrating agents), or with anhydrides or acid chlorides. Examples of such esters are 'nitroglycerine,' fats and oils.

Mix a few drops of glycerol with about five times as much benzoyl chloride and about 15 cc. of 10 per cent. caustic soda solution; shake the mixture for some minutes, cooling if necessary, and allow to stand. Add more soda drop by drop and shake until the odour of benzoyl chloride has disappeared. Allow to stand until solid separates. Filter, wash with water and then with *dilute* cold alcohol or acetic acid. Allow to dry and recrystallise from boiling petroleum ether. The glyceryl *di*benzoate so obtained melts at about 72°.

If a borax bead be immersed for a short time in an aqueous solution of glycerol, which has been made slightly alkaline with soda, and is then held in a Bunsen flame, the latter will be tinged with green.

Further, if to a dilute solution of borax, and a drop of phenol-phthalein, a solution of glycerol is added, the alkalinity of the borax disappears, the indicator becoming colourless. On warming the pink colour reappears, but fades again on cooling.

Free boric acid will scarcely liberate iodine from a mixture of iodide and iodate, but will do so if a drop of glycerol be added.

These reactions with borax and boric acid are also given by other polyhydric alcohols (such as glycol and mannitol), and to some extent by certain sugars.

When submitted to the action of certain oxidising agents, under appropriate conditions, glycerol may give rise to glyceraldehyde, dihydroxy-acetone, glyceric acid, tartronic acid, and further to glycollic, glyoxylic and oxalic acids, &c. If an aqueous solution of glycerol is mixed with a ferrous salt, and hydrogen dioxide is slowly added, in rather less than the calculated quantity, the liquid becomes hot and the solution will now contain glyceraldehyde $CH_2OH.CHOH.CHO$ (and perhaps some dihydroxy-acetone $CH_2OH.CO.CH_2OH$). The latter substances may be recognised, when the oxidation is completed, by adding phenylhydrazine acetate and allowing the mixture to stand; the brownish precipitate which

separates after washing and recrystallisation (from 50 per cent. alcohol and then from benzene) yields golden yellow prisms of glycerosazone ($CH_2OH.C(N_2HC_6H_5).CH(N_2HC_6H_5)$) which melt at 130—131°.

When glycerol is carefully heated to 120° with about an equal weight of phenol (fused) and of concentrated sulphuric acid, a brownish mass is obtained; if, after cooling, this is treated with water and a drop or two of ammonia, a carmine colour is produced.

A solution of glycerol mixed with a small quantity of pyrogallol and a few drops of strong sulphuric acid, boiled for a few seconds, cooled and diluted with alcohol, gives a purplish red coloration.

MANNITOL.

d **Mannitol. Mannite.** $C_6H_8(OH)_6$ or $CH_2OH.(CHOH)_4.CH_2OH$. [*Hexahydric alcohol.*]

White crystalline solid (needles or rhombic prisms). Slightly sweet taste. Easily soluble in water or in boiling alcohol; insoluble in ether. Its solution is optically inactive, but in presence of borax becomes dextro-rotatory. M. P. 166°.

With oxidising agents it may yield mannose, mannitic acid, saccharic acid, and further racemic and oxalic acids, but no mucic acid. (The isomer dulcitol yields mucic acid.)

Oxidised by hydrogen dioxide in presence of ferrous salts (see Glycerol) it gives rise to mannose $CH_2OH(CHOH)_4CHO$. The resulting solution when mixed with phenylhydrazine acetate gives a bulky orange precipitate; thus when washed with water and afterwards with a very little acetone, and recrystallised from boiling water, and from hot alcohol, is obtained in the form of yellowish crystalline plates; (by further recrystallisation from hot water with a little animal charcoal they become practically white). These crystals turn yellow at about 195° and melt at 197—198° [Mannose-hydrazone $CH_2OH.(CHOH)_4.CH(N_2HC_6H_5)$].

With borax mannitol behaves like glycerol.

ETHYL ETHER.

Ether. Diethyl oxide. $(C_2H_5)_2O$.

Colourless mobile liquid; very volatile and inflammable. B. P. 35°. Sp. gr. 0·719 at 15°. Miscible in all proportions with alcohol and most other organic solvents; with water the miscibility is limited (ether in water about 1 in 12, water in ether about 1 in 50 at ordinary temperatures). If pure it gives off no gas when treated with metallic sodium.

Dissolves fats, oils, resins, many alkaloids, &c.

FORMALDEHYDE.

Methyl aldehyde. H.CHO.

Colourless gas. Pungent irritating odour. [Liquifies at $-20°$, solidifies at $-90°$.] Commercial 'formalin' contains about 35—40 per cent of formaldehyde.

The aqueous solution on evaporation leaves a white residue of paraformaldehyde $(CH_2O)_x$ (x probably $= 3$). More marked if a drop of strong sulphuric acid is first added.

Conversely paraformaldehyde when heated (best in a current of some inert gas, such as nitrogen) yields gaseous formaldehyde. The same change also takes place when paraformaldehyde is heated with water, but the reaction is limited and reversible; the aqueous solution whether prepared from formaldehyde or paraformaldehyde will eventually contain both substances (perhaps also other polymers) in a ratio depending on the concentration, &c.

Formaldehyde, like other aldehydes, restores the colour to a solution of magenta (fuchsine) which has previously been just decolorised by sulphurous acid (Schiff's reaction); and gives a silver mirror, in the cold, with ammoniacal silver nitrate. It reduces Fehling's solution on warming.

Mixed with a strong solution of caustic soda (about twice normal) and hydrogen dioxide, it yields sodium formate, with evolution of hydrogen:—

$$2H.CHO + 2NaOH + H_2O_2 = 2H.COONa + 2H_2O + H_2.$$

[This reaction may be employed in certain cases for the quantitative estimation of formaldehyde, the excess of soda being determined by titration.]

An aqueous solution when saturated with hydrogen sulphide and warmed, or allowed to stand for some hours, and then mixed with strong hydrochloric acid and warmed, gives a shining white crystalline precipitate of trithioformaldehyde $(CH_2S)_3$; after recrystallisation (*e.g.* from hot acetone) this melts at 216°.

A precipitate can also be obtained with hydrogen sulphide alone without addition of acid; in this case the composition is $(CH_2S)_3.CH_2O$, and the melting point is lower. [Compare Acetaldehyde.]

Amongst the numerous colour-reactions* which have been recommended by various authors for the detection of formaldehyde the following may be mentioned:—

(*a*) When *dilute* solutions of formaldehyde and resorcinol† are mixed and then poured slowly on to concentrated sulphuric acid a red (or red-violet) ring is produced where the liquids meet, and on gently shaking red flocks appear.

(*b*) With *phloroglucinol* in alkaline solution it gives a red colour.

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* In making use of colour-reactions of this kind for the identification of unknown substances it is always advisable to compare the result with that given by the known pure substance under exactly similar conditions; the shade of colour will often largely depend on proportions, concentration, temperature, &c.

† If an alcoholic solution of gallic acid is used in place of resorcinol a beautiful blue colour is obtained.

Formaldehyde (*continued*).

(*c*) With a mixture of dilute solutions of sodium nitro-prusside and phenylhydrazine hydrochloride, followed by excess of caustic soda a deep blue colour is produced. (Acetaldehyde behaves similarly.)

Excess of formaldehyde when shaken with a *little* phenylhydrazine gives a bulky white precipitate which, after washing with water, alcohol and ether, and recrystallisation from a mixture of toluene and alcohol, is obtained in the form of lustrous rhombic plates melting at 183—184°. Other compounds however may be formed under varying conditions.

When a solution of formaldehyde is mixed with aqueous ammonia hexamethylenetetramine $C_6H_{12}N_4$ is produced. (This also affords a method for estimating formaldehyde, the residual ammonia being titrated.) By evaporation and purification of the product with alcohol, &c. the hexamethylenetetramine may be obtained in the crystalline state*. The characteristic odour of trimethylamine is generally noticed when the solution of formaldehyde and ammonia is evaporated. It has been shewn in fact that hexamethylenetetramine when heated with excess of formaldehyde yields trimethylamine.

ACETALDEHYDE.

Ethyl aldehyde. Aldehyde. $CH_3.CHO$.

Colourless mobile liquid. Pungent odour. B. P. 22°. Sp. gr. 0·79. Miscible in all proportions with water, alcohol and ether.

With Schiff's magenta reagent, ammoniacal silver nitrate and Fehling's solution it behaves like Formaldehyde.

Treated with hydrogen sulphide and hydrochloric acid it yields a white crystalline precipitate of trithioacetaldehyde $C_6H_{12}S_3$; but with hydrogen sulphide alone it gives only an oily product. [Compare Formaldehyde.]

Boiled with caustic soda the solution turns yellow and afterwards turbid, with separation of an orange or brown substance (aldehyde-resin), which has a penetrating disagreeable odour.

Treated with hydrogen dioxide and caustic soda it gives off an inflammable gas (? hydrogen), but more slowly than formaldehyde†.

If the solution is sufficiently strong and pure it will give a white crystalline precipitate ($CH_3.CH(OH).SO_3Na$) when shaken with excess of a strong solution of sodium hydrogen sulphite‡; it will also give a crystalline compound ($CH_3.CH(OH)NH_2$) if shaken with a few drops of strong (·880) ammonia.

When an aqueous solution of acetaldehyde is shaken with phenylhydrazine a white milky precipitate separates, which takes long to settle. The pure acetaldehyde-phenylhydrazone exists in two or more modifications, melting at different temperatures; for their isolation special conditions are necessary.

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* A characteristic property of hexamethylenetetramine is the formation of a deep orange or brick-red colour when it is exposed to the vapour of bromine; this colour is due to the tetrabromide. On exposure to the air it turns yellow, the dibromide being produced.

† This change has not been fully investigated. (Compare Geisow, *Ber.* 1904, 515.)

‡ This must be freshly prepared. Mix sodium bicarbonate with about three times its weight of water and pass in sulphur dioxide until all is dissolved.

CHLORAL.

Trichloracetaldehyde. $CCl_3 . CHO$.

Oily liquid. Penetrating odour. B. P. 97°. Sp. gr. 1·512 at 20°. When kept for some time, especially if not quite pure, it becomes changed to the solid polymer metachloral. With water it gives crystalline *chloral hydrate* $CCl_3 . CHO . H_2O$ or $CCl_3 . CH(OH)_2$. M. P. 57°. B. P. 97·5°. Soluble in about 1½ parts of water. Soluble also in alcohol, ether, benzene or carbon disulphide.

Mixed with caustic soda in aqueous solution it gives sodium formate with separation of chloroform,

$$CCl_3 . CHO + NaOH = H . COONa + CHCl_3.$$

Fehling's solution is reduced on heating, and a silver mirror may be obtained with ammoniacal silver nitrate. Schiff's magenta reaction is given by chloral, but not by chloral hydrate; in the other reactions mentioned the hydrate behaves like chloral itself.

ACETONE.

Dimethyl ketone. $CO(CH_3)_2$.

Colourless liquid. Peculiar odour. B. P. 56·3°. Sp. gr. 0·79 at 15°. Inflammable. Miscible in all proportions with water, alcohol or ether. Dissolves resins, fats, gums, camphor, &c.

With iodine and alkalis it yields the iodoform reaction. (See Ethyl Alcohol.)

Shaken with a concentrated solution, in excess, of sodium bisulphite (see page 110) it gives a crystalline precipitate of $(CH_3)_2C(OH) . SO_3Na$.

Mixed with an aqueous solution of hydroxylamine it yields acetoxime,

$$(CH_3)_2CO + NH_2OH = (CH_3)_2C : NOH + H_2O.$$

Take say 7·5 grams hydroxylamine hydrochloride and 8 c.c. acetone and mix with a solution of 4 grams caustic soda in 25 c.c. water, cooling and shaking. Allow mixture to stand 24 hours in a stoppered bottle or flask, and then extract the neutral solution with ether. Allow the ethereal solution to evaporate in a desiccator.

Acetoxime crystallises in colourless prisms, melting at 60°.

When acetone is mixed with a solution of sodium nitroprusside followed by caustic soda, a red colour is produced; this colour gradually fades and is changed to carmine by excess of glacial acetic acid. With a concentrated solution of sodium nitroprusside and a few drops of a solution of an aliphatic monamine (*e.g.* ethylamine), a magenta colour is obtained; this colour becomes more intense on standing, and is changed to blue or violet by glacial acetic acid. (If ammonia is employed in place of the amine a red or violet colour is slowly developed.) The nitroprusside solution should be freshly prepared.

ARABINOSE.

l. **Arabinose.** $C_5H_{10}O_5$ or $CH_2OH.(CHOH)_3.CHO$. [Class. *Carbohydrate. Monose. Aldo-pentose.*]

Small rhombic prisms. M. P. 159—160°. Dextrorotatory. Moderately soluble in cold water. Nearly insoluble in absolute ethyl alcohol; fairly soluble in hot methyl alcohol or 90 per cent. ethyl alcohol.

Reduces Fehling's solution on heating. Does not undergo alcoholic fermentation with yeast.

Phenylhydrazine acetate gives on heating a yellow precipitate of arabinosazone which when recrystallised from hot water and dried (over sulphuric acid) melts at 158—160°.

Boiled with hydrochloric acid (sp. gr. about 1·06) it gives rise to furfural $C_4H_3O.CHO$.* After the boiling has been continued for some time (best in a reflux apparatus) the product is distilled and the distillate tested with aniline acetate paper; a brilliant pink colour indicates the presence of furfural. [This test is considered to be characteristic of pentoses since they give a large yield of furfural; many other carbohydrates, however, will give the reaction.]

Heated with a saturated solution of phloroglucinol in hydrochloric acid (sp. gr. about 1·19) it gives a bright cherry-red colour.

DEXTROSE.

d. **Glucose. Grape sugar.** $C_6H_{12}O_6$ or $CH_2OH.(CHOH)_4.CHO$. [Class. *Carbohydrate. Monose. Aldo-hexose.*]

The anhydrous substance crystallises in rhombic prisms (usually indistinct) which melt at 144—146°. Easily soluble in water, but nearly insoluble in absolute ethyl or methyl alcohol. Fairly easily soluble in hot 90 per cent. alcohol. When hydrated it is generally obtained in the form of warty semi-crystalline masses; in this form it melts at about 80°, and is more easily soluble in ethyl or methyl alcohol.

Dextrorotatory. Less sweet than cane sugar. Dissolves in concentrated sulphuric acid without blackening; the solution blackens only slowly on heating. Heated with caustic alkalis it turns yellow and then brown. Heated for a short time with dilute acids it remains unchanged.

Reduces Fehling's solution and ammoniacal silver nitrate on heating.

A dilute aqueous solution when mixed with a solution of phenylhydrazine acetate* and heated on the water-bath gives after a short time (generally a few minutes) a yellow crystalline precipitate of glucosazone (phenyl glucosazone):—

$$CH_2OH.(CHOH)_3.CHOH.CHO + 3N_2H_3Ph = CH_2OH.(CHOH)_3.C(N_2HPh).CH(N_2HPh) + NH_2Ph + NH_3 + 2H_2O.$$

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* Mix equal volumes of 50 per cent. acetic acid and phenylhydrazine; the latter should be nearly colourless.

This precipitate, after washing with water and recrystallising from hot aqueous alcohol is obtained in the form of fine yellow needles which (quickly heated) melt usually at 204—205°. (By special treatment the melting point may be raised to 230—232°.)

In contact with yeast under favourable conditions it undergoes alcoholic fermentation:—

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2.$$

[Dissolve the sugar in about 5 parts of water, add a few drops of thin fresh brewer's yeast and keep the mixture at about 25°. Confirm carbon dioxide by allowing the evolved gases to pass into lime water. After the process has continued for some time, subject the mixture to distillation and test the first portions of distillate for ethyl alcohol by the iodoform reaction. A blank test should be made for comparison with yeast and pure water under the same conditions. If the experiment is performed on a sufficiently large scale the first portions of the distillate may be shaken with solid (dry) potassium carbonate; this removes the greater part of the water, and the strong alcohol which separates may be used for the other tests mentioned on pages 105—106.]

GALACTOSE.

d. **Galactose.** $C_6H_{12}O_6$ or $CH_2OH.(CHOH)_4.CHO$. [Class. *Carbohydrate. Monose. Aldo-hexose.*]

Microscopic needles or prisms, or hexagonal plates. M. P. 163—168°. Easily soluble in water or aqueous alcohol; nearly insoluble in methyl alcohol. Dextrorotatory. Reduces Fehling's solution and ammoniacal silver nitrate on heating. Undergoes alcoholic fermentation by action of certain yeasts, but more slowly than dextrose.

Phenylhydrazine acetate gives on heating a yellow precipitate of galactosazone; this crystallises from hot alcohol in yellow needles which (quickly heated) melt at 193—194°. (By special treatment the melting point can be raised to 214°.)

When oxidised by dilute nitric acid it gives a large yield of mucic acid. (See Milk sugar.)

LÆVULOSE.

d. **Fructose. Fruit sugar.** $C_6H_{12}O_6$ or $CH_2OH.(CHOH)_3.CO.CH_2OH$. [Class. *Carbohydrate. Monose. Keto-hexose.*]

Usually obtained in the form of hard crystalline masses. May be crystallised in rhombic prisms or needles. M. P. 95°. Very easily soluble in water. Soluble in boiling ethyl or methyl alcohol; also in a mixture of alcohol and ether. (Distinction from dextrose.)

Reduces Fehling's solution on heating rather more rapidly than dextrose.

In contact with yeast it undergoes alcoholic fermentation, but less readily than dextrose.

Heated with moderately dilute sulphuric acid, the solution soon darkens in colour with production of humus-like substances and of lævulinic acid, &c. Concentrated acids quickly char it. Boiled with strong aqueous hydrochloric acid it yields furfural. (Compare Arabinose.)

Lævulose (*continued*).

With phenylhydrazine acetate it yields glucosazone, identical with the product obtained from dextrose.

Treated with a concentrated solution of hydrogen bromide in dry ether it gives, after a short time, an intense purple colour; the colour is fully developed after the mixture has stood for about 30 minutes or less. [This reaction is only given by keto-hexoses or carbohydrates which produce them by hydrolysis (*e.g.* cane sugar or inulin); the other carbohydrates give a comparatively insignificant colour, and this only on long standing.] The colour is due to the formation of bromo-methyl-furfural $C_4H_2O(CH_2Br)CHO$.

If an aqueous solution of lævulose is mixed with a little ferrous sulphate, warmed to about 70—80° and hydrogen dioxide (not in excess) is then slowly added, a product is obtained which when heated with phenylhydrazine *p.* sulphonic acid, gives an orange-pink dye-stuff (for silk, &c.) which is very permanent. Aldose sugars similarly treated give a comparatively insignificant colour.

CANE SUGAR.

Saccharon. Saccharose. Sucrose. $C_{12}H_{22}O_{11}$. [Class. *Carbohydrate. Biose* or *Disaccharide.*]

Monoclinic crystals. Easily soluble in water. Fairly easily soluble in aqueous alcohol; nearly insoluble in absolute ethyl or methyl alcohol. M. P. 160—170°. Dextrorotatory.

Concentrated sulphuric acid blackens it at ordinary temperatures, causing it to swell up and evolve CO_2, SO_2, &c. with separation of carbon.

Heated with dilute acids it yields a mixture of equal quantities of dextrose and lævulose,

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

[Since lævulose is more powerfully lævorotatory than dextrose is dextrorotatory, the resultant mixture is called 'inverted sugar,' and the process is often referred to as 'inversion'; this term is likewise used for similar reactions in the case of other bioses, although there may be no change of sign in the rotatory power. The rate of inversion is greater as the acid is more ionised; *e.g.* greater for hydrochloric than for sulphuric acid (other things being equal) and is ascribed to the catalytic influence of hydrogen ions.]

Cane sugar does not reduce Fehling's solution, gives no reaction with phenylhydrazine acetate, and does not turn brown with alkalis. But if the action of these reagents is continued for a long time, a portion of the cane sugar may undergo inversion as above indicated and the resulting products will then give the reactions in question. Cane sugar itself is not directly fermentable by yeast; but in the latter an enzyme (invertase) is present which first produces dextrose and lævulose, and these then undergo alcoholic fermentation.

With dry hydrogen bromide in ethereal solution it behaves like lævulose, but the change is not quite so rapid.

MILK SUGAR.

Lacton. Lactose. $C_{12}H_{22}O_{11}.H_2O$. [Class. *Carbohydrate. Biose* or *Disaccharide.*]

Hard white crystalline mass (prisms). Less sweet than cane sugar; feels 'sandy' in the mouth. Becomes anhydrous at 130°; begins to turn brown at 170—180°, and melts at 203—204° to a brown liquid. Easily soluble in warm water; insoluble in absolute alcohol. Dextrorotatory. Concentrated sulphuric acid does not blacken it in the cold, but does so on heating.

Reduces Fehling's solution on heating, and readily gives a silver mirror with ammoniacal silver nitrate. Turns brown when heated with caustic alkalis.

Not directly fermentable by yeast, but readily undergoes lactic fermentation (*e.g.* in milk).

Heated with dilute acids it undergoes 'inversion,' giving dextrose and galactose. This change takes place less readily than in the case of cane sugar, requiring some hours for completion. Certain enzymes (*e.g.* emulsin) effect a similar transformation.

Heated with dilute nitric acid it first undergoes inversion, and is then oxidised to mucic and saccharic acids, &c.

[Heat 1 part of the sugar, on a water-bath, with about 12 parts of nitric acid, sp. gr. 1·15; evaporate to about ⅓ of its volume, cool, and add an equal volume of water. Mucic acid separates out on standing, and may be purified from any oxalic acid by treatment with warm alcohol.]

When an aqueous solution is mixed with phenylhydrazine acetate and heated for half an hour on a water-bath the liquid turns yellow, but no precipitate separates; after cooling and allowing to stand for some time a yellow crystalline precipitate of lactosazone appears. It may be re-crystallised from boiling water, in which it is fairly soluble, and is thus obtained in golden yellow needles which melt at 200°.

[The formula for lactosazone is $C_{24}H_{32}N_4O_9$, *i.e.* $C_{12}H_{22}O_{11} + 2N_2H_3C_6H_5 - 2H_2O - H_2$. Compare glucosazone.]

MALTOSE.

Malton. Amylon. Malt sugar. $C_{12}H_{22}O_{11}.H_2O$. [Class. *Carbohydrate. Biose* or *Disaccharide.*]

Crystallises in white needles or plates. Easily soluble in water, slightly soluble in alcohol. Becomes anhydrous when heated to 100°, and is then less soluble in alcohol. Dextrorotatory.

Concentrated sulphuric acid does not blacken it in the cold, but does so on heating. Turns brown when heated with caustic alkalis.

Maltose (*continued.*)

Reduces Fehling's solution on heating, but does not reduce cupric acetate (distinction from dextrose). Reduces ammoniacal silver nitrate. Fermentable by yeast.

Heated with dilute acids it slowly undergoes 'inversion,' giving two molecules of dextrose; the process is only complete after some hours. This inversion can also be brought about by certain enzymes, *e.g.* maltase. It has been shewn that this change is to some extent limited and reversible,

$$C_{12}H_{22}O_{11} + H_2O \rightleftharpoons 2C_6H_{12}O_6.$$

Heated on a water-bath, in aqueous solution, with phenylhydrazine acetate for half an hour it gives no precipitate, but the solution turns yellow; after cooling and allowing the solution to stand, a yellow crystalline precipitate of maltosazone ($C_{24}H_{32}N_4O_9$) separates. It is fairly soluble in boiling water, from which it crystallises in golden yellow needles melting at 190—191°.

STARCH.

$(C_6H_{10}O_5)_n$. [Class. *Carbohydrate. Higher polyose.*]

White tasteless powder. Insoluble in cold water. Heated with water the granules swell up, giving a nearly transparent mass (starch-paste). If more water is added to so-called starch, 'solution' is obtained which can be filtered. Moderately strong hydrochloric acid converts starch, after some days, into a modification which is soluble in water; this modification also results from the limited action of malt extract.

When heated to 110—210° it is converted into dextrin or British gum, which is easily soluble. This product is a mixture of no very definite composition (see below).

Boiled with dilute acids it is finally converted into dextrose; soluble starch, dextrins, maltose and isomaltose being intermediate products.

Starch-paste, or 'solution,' in contact with certain enzymes (*e.g.* diastase) undergoes a series of changes, the final products in this case being maltose and various dextrins; with ptyalin the change is similar, but some dextrose is said to be produced also.

Starch-paste, or 'solution,' gives an intense blue colour with iodine; the colour is discharged by heating, but reappears on cooling unless the solution is boiled for a long time. Alkalis, sulphurous acid, alcohol, &c. destroy the colour by removing the iodine. Fehling's solution is not reduced, and phenylhydrazine gives no reaction; alkalis do not turn it brown.

Glycogen is very similar to starch in most of its properties. With water it gives an opalescent solution which is dextrorotatory; the opalescence is removed by acetic acid. Iodine colours it red. It dissolves also in alkalis. On hydrolysis with acids or enzymes it behaves very similarly to starch.

Inulin is readily soluble in hot water. Its aqueous solution is lævorotatory. It is easily hydrolysed, giving as the principal product, *lævulose*. With hydrogen bromide it behaves like lævulose.

Dextrin is a name given to a considerable number of soluble substances having the empirical composition $C_6H_{10}O_5$, which are obtained from starch by the action of heat or of enzymes, &c. Some of these have been isolated as definite individuals, but the ordinary dextrins of commerce are of a more or less indefinite nature. They are white glassy friable substances very soluble in water, and insoluble in alcohol. On enzyme-hydrolysis most of them yield maltose, and their solutions are dextrorotatory. Ordinary dextrin is coloured reddish-brown by iodine. Heated with dilute sulphuric acid it eventually yields dextrose.

CELLULOSE.

$(C_6H_{10}O_5)_n$.

Principal constituent of plant tissues. Occurs in a variety of forms. The name cellulose is used in a wide sense to denote a large group of substances, and should not be understood to refer to a single individual chemical compound. Provisionally cellulose is classified as a carbohydrate and as a higher polyose. In its commoner forms (*e.g.* Swedish filter paper, cotton wool) it is a white fibrous substance which contains variable amounts of hygroscopic moisture.

Insoluble in all ordinary solvents. May be dissolved by a concentrated solution of zinc chloride (40 per cent.) on heating, or in a cold mixture of zinc chloride and hydrochloric acid. When the resulting solution is poured into water or alcohol, cellulose again separates as a hydrate or a compound with zinc oxide.

Ammoniacal cupric oxide* also dissolves it; from this solution acids, salts, sugar, &c. precipitate a gelatinous hydrate.

Dissolves gradually in cold concentrated sulphuric acid with production of a series of sulphates $C_{6n}H_{10n}O_{5n-x} . xSO_4$; these are easily hydrolysed by water, yielding 'colloidal' cellulose (amyloid), dextrins or dextrose according to the extent of action of the acid, &c.

[Treat 5 parts cellulose with a cold mixture of 25 parts concentrated sulphuric acid and 8½ parts water (by weight). Stir together and allow to stand until the mixture is completely dissolved, dilute considerably with water and boil for about 3 hours. Neutralise with chalk or barium carbonate and test resulting solution for dextrose.]

Iodine alone does not give a blue colour; it does so however in presence of certain dehydrating agents such as zinc chloride†.

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* Schweitzer's reagent. To a solution of cupric sulphate add ammonium chloride and then excess of caustic soda; wash ppt. thoroughly and dissolve it in ammonia (sp. gr. about 0·92).

† Schulze's reagent. To 100 c.c. of a solution of zinc chloride (sp. gr. 1·8) add 6 grams potassium iodide and 6 grams iodine.

Cellulose (*continued.*)

Hydrochloric acid or dilute sulphuric acid converts it after a time into a friable substance which appears to be more reactive and more soluble than the original cellulose; this product is often called 'hydrocellulose,' and is considered by some to have the formula $C_{12}H_{22}O_{11}$.

By action of oxidising agents (HNO_3, H_2O_2, CrO_3, &c.) under certain conditions, products are obtained, termed 'oxycellulose,' which dissolve in alkalis. For these such formulæ as $C_{18}H_{26}O_{16}$ and $C_{36}H_{60}O_{31}$ have been given.

Strong nitric acid in presence of strong sulphuric acid gives a series of cellulose nitrates, *e.g.* $C_6H_7O_2(NO_3)_3$ gun-cotton.

Heated with hydrogen bromide in closed vessels it gives bromo-methyl-furfural. (Compare Lævulose.)

FORMIC ACID.

H.COOH. [*Monobasic acid.* $C_nH_{2n+1}.COOH$ *series.* ($n = 0$).]

Colourless liquid; sharp penetrating odour. M. P. 8·6°. B. P. 101°. Sp. gr. 1·23 at 10°. Acts as a powerful reducing agent on salts of Hg, Ag, Pt, &c. and on alkaline permanganate. (Distinction from acetic acid.) Shaken with mercuric oxide it gives a solution of mercuric formate; this on heating gives first a precipitate of mercurous formate and, on further heating, metallic mercury, half the formic acid being liberated,

$$2(H.COO)_2Hg'' = 2H.COOHg' + H.COOH + CO_2,$$

and

$$2H.COOHg = 2Hg + H.COOH + CO_2.$$

A dilute solution of formic acid when treated with metallic magnesium yields a certain quantity of formaldehyde which can easily be identified by the tests given on pages 109, 110.

For other reactions see page 43.

ACETIC ACID.

CH_3.COOH. [*Monobasic acid.* $C_nH_{2n+1}.COOH$ *series.*]

Colourless. Penetrating odour. Miscible in all proportions with water, alcohol or ether. M. P. 16·5—17°. B. P. 118°. Sp. gr. 1·05 at 15°. Glacial acetic acid solidifies to a crystalline mass in cold weather; it may be purified by draining the crystals and repeatedly melting and freezing, draining the crystals each time.

For reactions see page 42.

PALMITIC ACID and STEARIC ACID.

$C_{15}H_{31}.COOH$ (M. P. 62°) $C_{17}H_{35}.COOH$ (M. P. 69°).

[*Monobasic acids.* $C_nH_{2n+1}.COOH$ *series.*]

Colourless waxy solids. Insoluble in water or dilute acids. Soluble in alcohol, ether, carbon disulphide, &c. May be crystallised from hot alcohol. The sodium and potassium salts dissolve in pure water; the free acids are precipitated on addition of dilute HCl. The calcium, magnesium lead, &c. salts are insoluble. Commercial 'Stearine' consists principally of a mixture of these two acids.

OLEIC ACID.

$C_{17}H_{33}.COOH$. [*Monobasic acid.* $C_nH_{2n-1}.COOH$ *series.*]

Colourless oily liquid. M. P. 14°. Sp. gr. 0·89 at 20°.

Insoluble in water. Easily soluble in alcohol, ether, carbon bisulphide, &c. An alcoholic solution of the pure acid is neutral to indicators. The potassium and sodium salts are soluble in pure water and in alcohol. The normal lead salt is insoluble in water, but dissolves in alcohol and ether.

Being an unsaturated acid it immediately discolorises an alkaline solution of potassium permanganate; it also combines directly with bromine, discharging the colour of the latter from its solution in some inert solvent (*e.g.* carbon tetrachloride).

When subjected to the action of oxides of nitrogen (*e.g.* from arsenious oxide and nitric acid) in the cold, it yields a crystalline mass of elaïdic acid $C_{17}H_{33}.COOH$ (isomeric with oleic acid), which after recrystallisation from alcohol melts at 47—51°.

When fused with caustic potash at about 300° it yields a mixture of acetate and palmitate.

LACTIC ACID.

α. Hydroxypropionic acid. r. Lactic acid. Fermentation lactic acid.

$CH_3.CH(OH).COOH$. [*Monobasic hydroxy-acid.* $C_nH_{2n}(OH)COOH$ *series.*]

As generally met with it is a colourless syrupy liquid. The pure acid can be crystallised, and melts at 18°. Miscible with water, alcohol or ether. Optically inactive. Metallic lactates are all soluble in water. The zinc salt $Zn(C_3H_5O_3)_2.3H_2O$ is somewhat sparingly soluble, and crystallises in needles. The lead salt is soluble in alcohol.

Lactic acid (*continued.*)

Heated with concentrated sulphuric acid it turns brown and evolves carbon monoxide; distilled with moderately strong sulphuric acid it yields acetaldehyde. Potassium permanganate is discolorised in either acid or alkaline solution. Fehling's solution is not reduced. Like many other hydroxy-acids it gives a yellow colour with ferric chloride in the cold.

When carefully oxidised by hydrogen dioxide in presence of a ferrous salt at 0° it yields pyruvic acid $CH_3.CO.COOH$, which is easily identified by its hydrazone (M. P. 192°).

Sarcolactic acid closely resembles the above acid, but it is dextrorotatory, and its zinc salt, which crystallises with $2H_2O$, is more soluble.

OXALIC ACID.

$$\begin{array}{l} COOH \\ \dot{C}OOH \end{array}. \quad [\textit{Dibasic acid.}]$$

The crystallised acid, $C_2H_2O_4.2H_2O$ (monoclinic prisms) is fairly easily soluble in water and alcohol; slightly soluble in ether. M. P. 99—100°. Becomes anhydrous when carefully heated to 60—70°, and may then be sublimed unchanged at about 150°. Quickly heated it partly decomposes into formic acid, carbon monoxide, carbon dioxide and water.

Heated with glycerol the crystallised acid yields formic acid and carbon dioxide.

For other reactions see page 29.

SUCCINIC ACID.

$$\begin{array}{l} CH_2.COOH \\ \dot{C}H_2.COOH \end{array}. \quad [\textit{Dibasic acid.} \quad C_nH_{2n}(COOH)_2 \ \textit{series.}]$$

Colourless monoclinic prisms or plates. Somewhat sparingly soluble in cold water; easily soluble in hot water or alcohol, sparingly soluble in ether. M. P. 182°. Quickly heated to about 235° it vaporises with loss of water yielding succinic anhydride $C_2H_4\left\langle\begin{array}{l} CO \\ CO \end{array}\right\rangle O$ (needles slightly soluble in water. M. P. 120°).

Solutions of neutral succinates if not too dilute give with *silver nitrate, lead acetate* and *calcium chloride* white ppts. of the corresponding normal salts.

Ferric chloride (neutral) a bulky brown ppt. of basic ferric succinate

$$Fe_2(C_4H_4O_4)_3.Fe(OH)_3 \ [\text{or } Fe(C_4H_4O_4)(OH)].$$

If this ppt. is washed and boiled with ammonia it is decomposed, partly or entirely, into ferric hydroxide and ammonium succinate; the filtered solution gives with barium chloride and alcohol a white ppt. of barium succinate. (Distinction from benzoic acid, &c.)

MALIC ACID.

Hydroxysuccinic acid. $COOH.CHOH.CH_2.COOH$. [*Hydroxy-dibasic acid.*]

Colourless deliquescent prisms. Very easily soluble in water and in alcohol. Lævorotatory in dilute solution; dextrorotatory in concentrated solution, but becoming lævorotatory on addition of acids. M. P. 100°. Heated to about 140° it slowly yields fumaric acid. Rapidly heated to 200° maleic anhydride is produced; the latter sublimes in crystals which when recrystallised from hot water give maleic acid. M. P. 130°.

When oxidised by hydrogen dioxide in presence of ferrous salts it yields oxalacetic acid $COOH.CO.CH_2.COOH$.

Dissolve malic acid in the least possible quantity of water, add a few drops of ferrous sulphate solution, cool to about 0° and *very gradually* add hydrogen dioxide (20 vol.) in less than the molecular proportion (about 3 c.c. for 1 gram of the acid). Note the intense red colour, due to the action of oxalacetic acid on ferric salt; addition of ferric chloride intensifies the colour. If excess of phenylhydrazine acetate is added to the mixture an orange yellow precipitate is obtained (Nastvogel's osazone). (See Tartaric acid.)

Solutions of malates give with

Lead acetate a bulky white ppt. of lead malate; this is soluble in warm acetic acid. (Distinction from tartaric, citric and oxalic acids.)

Calcium chloride no ppt. even on boiling except in very concentrated solutions, or on addition of alcohol.

TARTARIC ACID.

Dextro-tartaric acid. Dihydroxysuccinic acid. $COOH.CHOH.CHOH.COOH$.
[*Dihydroxy-dibasic acid.*]

Monoclinic prisms. Easily soluble in water and alcohol, very slightly soluble in ether. M. P. about 170°. When further heated it yields anhydrides ($C_8H_{10}O_{11}$, $C_4H_4O_5$, &c.), pyruvic acid, pyrotartaric acid and other products, and carbonises, giving an odour of burnt sugar.

When oxidised with hydrogen dioxide in presence of ferrous salts it yields dihydroxymaleic acid $COOH.C(OH):C(OH).COOH$.

Proceed as directed in the case of malic acid. Test one portion of the resulting solution with excess of caustic soda; observe the deep violet colour, which is intensified by addition of ferric chloride. To another portion add excess of phenylhydrazine acetate and warm; an orange precipitate is produced of Nastvogel's osazone $CH(N_2HC_6H_5).C(N_2HC_6H_5).COOH$. Wash ppt. with water, allow to dry in the air and recrystallise several times from boiling chloroform. (Orange-yellow prisms. M. P. 222—224°.)

For reactions of tartrates see page 33.

Racemic acid is distinguished from ordinary tartaric acid by its higher melting point (about 206°), its optical inactivity and the insolubility of its calcium salt in acetic acid or in ammonium chloride.

MUCIC ACID.

Tetrahydroxyadipic acid. COOH.(CHOH)$_4$.COOH. [*Tetrahydroxy-dibasic acid.*]

Colourless crystalline powder. Nearly insoluble in cold water (1 in 300). Slightly soluble in boiling water (1 in 60). Optically inactive. M. P. 214°. Further heated it yields pyromucic acid $C_4H_3O.COOH$ and dehydromucic acid $C_4H_2O(COOH)_2$. Long boiling with much water converts it into a soluble lactone (so-called paramucic acid).

Dissolves in alkalis forming mucates; the acid salts are often more soluble than the normal salts.

When ammonium mucate is heated to about 200° it yields pyrrol C_4H_5N.

Treat a small quantity of mucic acid with strong ammonia, evaporate to dryness, heat residue in a test-tube and test the evolved vapours with a piece of pine wood which has been dipped into strong HCl; an intense red colour is produced if pyrrol is present.

When shaken with water and treated with a ferrous salt and a very small quantity of hydrogen dioxide followed by excess of caustic alkali a red or violet colour is obtained, which is somewhat intensified by addition of ferric chloride.

CITRIC ACID.

Hydroxytricarballylic acid. COOH.CH$_2$.C(OH)(COOH).CH$_2$COOH.
[*Hydroxy-tribasic acid.*]

Transparent colourless prisms. Easily soluble in water or alcohol; nearly insoluble in ether. The ordinary crystals contain one molecule of water. M. P. 100°. The dry acid melts at 153°. Further heated it yields aconitic acid $C_3H_3(COOH)_3$; at a higher temperature it gives acetone, itaconic acid, citraconic anhydride, &c. It also gives acetone when heated with dilute sulphuric acid and potassium permanganate.

When dry citric acid is heated for some time to about 180° with an equal weight of resorcinol and a few drops of concentrated sulphuric acid it yields a product (resocyanin $C_{21}H_{18}O_6$) which dissolves in alkalis, giving a solution which has a blue fluorescence.

For reactions of citrates see page 34.

ETHYL ACETATE.

Acetic ester. 'Acetic ether.' CH$_3$.COO(C$_2$H$_5$). [*Ester.*]

Colourless mobile liquid. Fragrant agreeable odour. B. P. 77°. Sp. gr. 0·907 at 15°. Miscible in all proportions with alcohol, ether, acetic acid or chloroform; with water the miscibility is limited (the ester in water 1 in 9, and of water in the ester 1 in 24, at

ordinary temperatures). A solution of ethyl acetate in water saturated at ordinary temperature becomes turbid on warming, since it is more soluble in cold than in hot water.

Heated with caustic alkalis in aqueous solution it is readily 'saponified,'

$$CH_3.COO(C_2H_5) + KOH = CH_3.COOK + C_2H_5OH.$$

[The rate at which this change takes place, other things being equal, depends upon the 'strength' of the base, *i.e.* the concentration of the OH ions.]

Heat ethyl acetate to boiling with about 3 times its volume of strong aqueous soda (about 1 in 3 or 4) in a flask fitted with an upright condenser for about half an hour (or until the odour of ethyl acetate disappears). Distil off the portion which comes over below 100°. Treat the distillate with solid potassium carbonate (to remove most of the water), and examine the liquid for *ethyl alcohol*. Confirm *acetate* in the residue by distilling with strong sulphuric acid.

FATS and OILS.

[*Esters.*]

The natural fats and oils are mixtures of the glyceryl esters of certain acids of the $C_nH_{2n+1}.COOH$ and $C_nH_{2n-1}.COOH$ series, *e.g.* glyceryl stearate (or Tristearin) $(C_{17}H_{35}COO)_3C_3H_5$, glyceryl palmitate (or Tripalmitin) $(C_{15}H_{31}COO)_3C_3H_5$, glyceryl oleate (or Trioleïn) $(C_{17}H_{33}COO)_3C_3H_5$. Mutton fat consists largely of tristearin, tallow and lard of tripalmitin and tristearin with some trioleïn, and olive oil principally of trioleïn. The fats and oils are generally lighter than water; insoluble in water, soluble to some extent in alcohol, and easily soluble in ether, chloroform, benzene, carbon disulphide, &c.

By action of caustic soda or potash they are easily saponified, giving the sodium or potassium salt of the acid (soaps) and glycerol, *e.g.*

$$(C_{17}H_{35}COO)_3C_3H_5 + 3NaOH = 3C_{17}H_{35}COONa + C_3H_5(OH)_3.$$

Boil lard or mutton fat with about 4 or 5 times its weight of strong caustic soda solution (1 in 2) in an iron vessel for half an hour. Allow to cool; the soap mostly separates, being sparingly soluble in strong soda solution (more may be separated by 'salting out,' see page 65), the glycerol remaining in solution. Evaporate solution on a water-bath to small bulk and mix with anhydrous sodium sulphate, or lime, so as to give a semi-solid mass. Extract with a mixture of equal volumes of ether and alcohol (or with acetone), evaporate the solution so obtained and test residue for glycerol (page 107).

When boiled with lead oxide and water a similar change occurs, *e.g.* with olive oil:—

$$2(C_{17}H_{33}COO)_3C_3H_5 + 3PbO + 3H_2O = 3(C_{17}H_{33}COO)_2Pb + 2C_3H_5(OH)_3.$$

Boil olive or almond oil with about twice its weight of lead oxide and five or six parts of water, as above, for about an hour or more, adding more water when necessary. Test aqueous solution for glycerol and examine the properties of the lead salt (lead plaster).

The saponification of fats and oils may be still more readily effected by potash in methyl alcohol.

Fats or oils containing oleïn are distinguished from those derived only from acids of the $C_nH_{2n+1}.COOH$ series by their power of decolorising a solution of bromine (or iodine, slowly) in an inert solvent such as carbon tetrachloride.

METHYLAMINE and ETHYLAMINE.

$NH_2(CH_3)$ $NH_2(C_2H_5)$.

[*Primary mon-amines.*]

Methylamine is a gas at ordinary temperatures (B. P. $-6°$) and ethylamine is a colourless liquid, B. P. 19°. They have a powerful ammoniacal odour, and turn red litmus blue.

For the following reactions the ordinary 33 per cent. aqueous solutions may be employed.

When mixed with hydrochloric acid and evaporated on a water-bath a white crystalline residue of the hydrochloride is obtained which may be recrystallised from hot alcohol.

An aqueous solution of the hydrochloride, if not too dilute, gives with hydrochloroplatinic acid a yellow or orange crystalline precipitate of the corresponding salt,

$$(NH_2CH_3 . H)_2PtCl_6 \text{ or } (NH_2C_2H_5 . H)_2PtCl_6.$$

With chloroform and alcoholic potash they give the carbamine reaction (see Chloroform).

With copper sulphate they behave like ammonia, giving a blue precipitate soluble in excess to a deep blue solution.

Nitrous acid gives free nitrogen and the corresponding alcohol,

$$NH_2CH_3 + HNO_2 = CH_3OH + H_2O + N_2.$$

[Mix the hydrochloride in aqueous solution with about the calculated quantity of sodium nitrite, and pour the solution slowly into glacial acetic acid; observe the evolution of nitrogen and test residual liquid for the alcohol.]

With sodium nitroprusside and acetone they give a magenta colour which increases on standing, and is changed to blue or violet by acetic acid (see Acetone).

ACETAMIDE.

$CH_3 . CONH_2$. [*Mon-amide.*]

Colourless deliquescent crystals. M. P. 82°. B. P. 222°. Easily soluble in water or alcohol, sparingly soluble in ether or benzene. The pure substance is practically odourless, but the ordinary specimens have a 'mouse-like' odour due to impurity.

Heated with caustic soda it evolves ammonia with formation of sodium acetate,

$$CH_3 . CONH_2 + NaOH = CH_3COONa + NH_3.$$

With bromine and caustic soda, or with bleaching powder, it yields methylamine; the final change may be represented as

$$CH_3 . CONH_2 + O = CH_3 . NH_2 + CO_2.$$

This reaction may be observed on a small scale by distilling a small quantity of acetamide with bleaching powder and excess of calcium hydroxide made into a paste with water.

With acids, acetamide forms unstable salts which are easily hydrolysed; the nitrate $CH_3CONH_2 . HNO_3$ for example can be prepared by dissolving acetamide in strong nitric acid. On the other hand acetamide may exhibit acidic properties, one atom of hydrogen being replaceable by metals; an aqueous solution when boiled with mercuric or silver oxides gives the compounds $(CH_3CONH)_2Hg$ and $CH_3CONHAg$.

When distilled with phosphorus pentoxide it gives rise to acetonitrile $CH_3 . CN$

UREA.

Carbamide. $CO(NH_2)_2$. [*Di-amide.*]

Colourless prisms resembling potassium nitrate in appearance. M. P. 132°. Easily soluble in water, somewhat sparingly soluble in cold alcohol (about 1 in 20 at ordinary temperature), nearly insoluble in ether. In aqueous solution it 'reverts' to a small extent to ammonium cyanate NH_4CNO.

Heated over a small flame, in a test-tube, to about 150° it first fuses, gives off ammonia freely, and then solidifies again, forming biuret,

$$2CO(NH_2)_2 = NH_2.CO.NH.CO.NH_2 + NH_3.$$

If this product is dissolved in cold caustic soda and mixed with a drop of copper sulphate a characteristic red-violet colour is produced.

On further heating cyanuric acid $H_3C_3N_3O_3$ and other products are obtained.

Strong nitric acid gives, in solutions which are not too dilute, a white crystalline precipitate of urea nitrate $CO(NH_2)_2.HNO_3$. The crystalline oxalate $[CO(NH_2)_2]_2.C_2H_2O_4.2H_2O$ is similarly obtained.

Boiled with caustic soda, it evolves ammonia,

$$CO(NH_2)_2 + 2NaOH = Na_2CO_3 + 2NH_3.$$

Sodium hypobromite in presence of caustic soda causes a rapid evolution of nitrogen:—

$$CO(NH_2)_2 + 3NaBrO + 2NaOH = 3NaBr + Na_2CO_3 + 3H_2O + N_2.$$

[Under ordinary conditions there is a deficiency of about 7 or 8 per cent. of the nitrogen evolved.]

Sodium hypochlorite in presence of excess of caustic soda evolves only half the nitrogen, the other half remaining as cyanate:—

$$2CO(NH_2)_2 + 3NaClO + 2NaOH = 2NaCNO + 3NaCl + 5H_2O + N_2.$$

[Under certain conditions, hydrazine N_2H_4 can be obtained by the action of hypochlorites on urea.]

Nitrous acid (or a nitrite + dilute H_2SO_4) evolves nitrogen and carbon dioxide, the reaction being completed on heating,

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 3H_2O + 2N_2.$$

Mercuric nitrate gives (in absence of chlorides) a white ppt. of $2CO(NH_2)_2.3HgO.Hg(NO_3)_2$; the composition may, however, vary according to conditions.

'Methyl-furil'* when mixed with solid urea and a few drops of phosphorus oxychloride (acetylchloride or dry HCl in acetic acid may be used instead) gives an intense and brilliant blue colour. Solutions of urea should be mixed with an alcoholic solution of the reagent

* See note on page 149.

and allowed to evaporate (at a gentle heat) to dryness before adding the $POCl_3$, &c. The same effect may be observed by dipping 'methyl-furil' test-paper in a solution of urea in concentrated HCl, but the reaction is then less delicate, and the colour is more slowly developed.

When urea is mixed with metallic sodium and heated to deflagration the sodium derivative of cyanamide is obtained,

$$CO(NH_2)_2 - H_2O = NH_2.CN.$$

If the product is extracted with water and mixed with ammonia (in sufficient excess) and silver nitrate, a yellow precipitate of silver cyanamide is obtained.

BENZENE.

Benzol. C_6H_6. [*Cyclic hydrocarbon.*]

Colourless liquid. B. P. 80·3°. Sp. gr. 0·874 at 20°. Solidifies when cooled to about 0°, giving rhombic prisms. M. P. 5·4—6°.

Highly inflammable; burns with a smoky luminous flame.

Miscible with most organic solvents, but insoluble in water. Dissolves many fats, waxes, india-rubber, &c.

Pure benzene should not darken when shaken for a short time with concentrated sulphuric acid, and should not quickly decolorise bromine. The presence of thiophene C_4H_4S, may be detected by adding isatin dissolved in strong sulphuric acid, which will give a blue colour if thiophene is present.

By action of strong nitric acid it yields nitrobenzene,

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$

This change may be illustrated on a small scale by slowly mixing benzene with rather more than an equal volume of fuming nitric acid, not allowing the temperature to rise above about 50°, and pouring the resulting mixture into a large volume of water.

On a larger scale a well cooled mixture of strong nitric acid, sp. gr. 1·4 (10 parts) and concentrated sulphuric acid (15 parts) is slowly run into benzene (5 parts); the temperature during mixing must not be allowed to rise above 50 or 60°, but the mixture may afterwards be heated on a water-bath.

By varying the conditions *dinitrobenzene* $C_6H_4(NO_2)_2$ (chiefly meta) may be obtained: mix as before 25 c.c. nitric acid (sp. gr. 1·42) and 25 c.c. concentrated sulphuric acid with 12 c.c. benzene, shake well and add 50 c.c. more of concentrated sulphuric acid, heat for some time to about 120°, cool and pour into water.

By action of sulphuric acid it yields benzene-sulphonic acid,

$$C_6H_6 + H_2SO_4 = C_6H_5.SO_3H + H_2O.$$

Gradually add 5 c.c. of benzene to 10 c.c. of fuming sulphuric acid, keeping the temperature below 50° and constantly shaking. Pour the mixture into about 40 c.c. of water, cool, filter if necessary, partly neutralise with sodium carbonate, add about 10 grams of sodium chloride and warm until it is dissolved. On cooling the sodium salt of benzene-sulphonic acid separates in crystalline plates.

NAPHTHALENE.

$C_{10}H_8$. *Cyclic Hydrocarbon (with condensed nucleus.)*

Colourless crystalline plates. M. P. 79—80°. B. P. 218°. Insoluble in water. Sparingly soluble in cold alcohol, easily soluble in hot alcohol, ether, glacial acetic acid, &c. Burns with smoky flame. Vaporises considerably below its boiling point. Characteristic odour.

Treated with bromine it yields torrents of hydrogen bromide gas, substitution taking place and bromonaphthalenes being formed.

Heated with about twice its weight of picric acid in alcohol solution it gives rise to naphthalene picrate $C_{10}H_8 . C_6H_2(NO_2)_3OH$, which separates on cooling in long golden-yellow needles; after draining and washing carefully two or three times with a little cold alcohol, the crystals melt at 149—150°.

Treated with about 4 times its weight of nitric acid (sp. gr. 1·33) and allowed to stand for some days it gives rise in part to α. nitronaphthalene $C_{10}H_7(NO_2)$.

After diluting the mixture with water, washing and drying the precipitate, treating with a little alcohol and dissolving in carbon disulphide, filtering from dinitronaphthalene, evaporating (carefully) and recrystallising the product from alcohol, the nitronaphthalene is obtained in the form of yellow needles. M. P. 61°.

NITROBENZENE.

$C_6H_5 . NO_2$.

Pale yellow liquid having an odour of bitter almonds. B. P. 206—209°. Sp. gr. 1·208 at 15°. When pure it may be solidified by cooling, and the crystals so obtained melt at 5°. Miscible with alcohol, ether, benzene, &c. Strong nitric and sulphuric acids convert it to a mixture of dinitrobenzenes.

Reducing agents such as hydrogen sulphide, or zinc, tin, iron, &c. with acids, convert it into aniline,

$$C_6H_5NO_2 + H_2 = C_6H_5NH_2 + H_2O.$$

Mix 25 grams nitrobenzene with 45 grams of metallic tin and about 100 c.c. of strong hydrochloric acid. Add the acid in small quantities at a time, cooling if necessary to moderate the action. Heat on a water bath until the odour of nitrobenzene disappears. Add excess of caustic soda and distil off the aniline in steam.

Meta dinitrobenzene $C_6H_4(NO_2)_2$ crystallises in colourless needles. M. P. 91°. B. P. 297°. Nearly insoluble in water, easily soluble in hot alcohol.

PHENOL.

Hydroxybenzene. 'Carbolic Acid.' $C_6H_5.OH$.

Colourless crystalline mass. M. P. 43°. B. P. 183°. Characteristic odour of phenols; poisonous; antiseptic. Slightly soluble in water at ordinary temperatures (1 in 10·7, by weight, at 20°), but miscible in all proportions above 68·4°. Miscible with alcohol, ether, benzene, acetic acid, &c. in all proportions. Forms crystalline hydrates with water. Turns red when exposed to the air.

By action of nitric acid, under varying conditions, mono-, di- or tri-nitrophenols are produced.

Dissolve phenol in about an equal weight of concentrated sulphuric acid, warming gently; this produces phenol-sulphonic acid. Add the mixture *very gradually* to about twice its volume of strong nitric acid, shaking and warming. If an oil separates add a few drops of fuming nitric acid, and again warm on a water-bath. Pour the mixture into cold water. Yellow crystals of trinitrophenol $C_6H_2(NO_2)_3.OH$ (Picric acid) separate; after recrystallisation from dilute hydrochloric acid these melt at 122—123°. The fused acid, and many picrates, are explosive. Picric acid dissolves in water to a yellow solution which dyes wool an intense yellow colour. The pure acid appears to be colourless, the yellow colour being due to ionisation. With dextrose and caustic soda it gives a brown colour, and with potassium cyanide a violet solution and a brown precipitate (isopurpuric acid).

When phenol is dissolved in strong sulphuric acid containing a small quantity of a nitrite, or of a nitroso-compound, it gives a red or brown colour which turns blue or green on warming; if this is poured into water a red colour is obtained which turns blue or green on addition of alkali. (Liebermann's reaction for nitroso-compounds and for many phenols.)

With benzoyl chloride and caustic soda (see page 148) it yields phenyl benzoate $C_6H_5COOC_6H_5$, which when recrystallised from a little alcohol melts at 69°.

An aqueous solution of phenol gives the following reactions:—

Bromine water in excess gives, even in very dilute solutions of phenol, a white precipitate of tribromo-phenol $C_6H_2Br_3.OH$.

Ferric chloride gives a violet colour, which is destroyed by acids. When mixed with dilute ammonia and a little sodium hypochlorite, or bleaching powder, a blue colour is produced.

HYDROQUINONE.

para Dihydroxybenzene. Quinol. $C_6H_4(OH)_2$. [*Dihydric phenol.*]

Colourless prisms or leaflets. M. P. 169°. Sparingly soluble in cold water; easily soluble in alcohol, ether or hot water.

An aqueous solution gives with ferric chloride a dark green crystalline precipitate of quinhydrone $C_6H_4O_2.C_6H_4(OH)_2$. Addition of more ferric chloride and heating oxidises this to quinone:—

$$C_6H_4(OH)_2 + 2FeCl_3 = C_6H_4O_2 + 2FeCl_2 + 2HCl.$$

[Quinone crystallises in golden yellow prisms. M. P. 116°. Easily soluble in alcohol, ether or hot water.]

Hydroquinone reduces ammoniacal silver nitrate in the cold and alkaline cupric oxide on warming; it also acts as a photographic developer.

Resorcinol (Resorcine) is *meta* dihydroxybenzene. Colourless prisms. M. P. 119°. Easily soluble in water.

Ferric chloride gives a violet colour, and bromine water a white precipitate of the tribromo-derivative. It reduces Fehling's solution or ammoniacal silver nitrate.

Heated with phthalic anhydride it gives rise to fluorescein $C_{20}H_{12}O_5$.

Heat resorcinol with about half its weight of phthalic anhydride for a short time over a small flame to about 200° (or with phthalic acid and a drop of sulphuric acid to about 160°). Cool and dissolve the product in caustic soda; on pouring the solution into water a brilliant yellowish green fluorescence will be observed.

Resorcinol in presence of hydrochloric acid gives characteristic colour-reactions with aldehydes, &c. and, in presence of strong sulphuric acid, with many acids.

Pyrocatechol (Catechol or Pyrocatechin) is *ortho* dihydroxybenzene. Colourless plates. M. P. 104°. Easily soluble in water, alcohol or ether. Reduces Fehling's solution or ammoniacal silver nitrate in the cold, and acts as a photographic developer.

Ferric chloride gives a green colour which changes to violet or red on addition of sodium bicarbonate.

Lead acetate gives a white precipitate.

PYROGALLOL.

1. 2. 3 Trihydroxybenzene. 'Pyrogallic acid.' $C_6H_3(OH)_3$. [*Trihydric phenol.*]

White leaflets or needles. M. P. 132°. Extremely easily soluble in water, fairly easily soluble in alcohol or ether. Its solution in aqueous alkalis rapidly turns brown when exposed to air. It quickly reduces copper, silver or mercury salts, and acts as a photographic developer.

Ferric chloride gives a red colour and ferrous sulphate containing a little ferric chloride a deep blue colour.

Heated with acetic anhydride and a little dry sodium acetate it yields the triacetate $C_6H_3(CH_3CO_2)_3$. After treatment with water and recrystallisation from alcohol this melts at 161—162°.

Phloroglucinol in *1. 3. 5* trihydroxybenzene (behaving sometimes like a triketo compound). Large colourless prisms containing $2H_2O$, which is lost at 100°. M. P. 218° when quickly heated. Easily soluble in water, alcohol or ether.

Ferric chloride gives a deep violet colour which soon fades.

A pine-wood splinter which has been dipped in strong HCl is coloured deep cherry-red by phloroglucinol solution.

BENZALDEHYDE.

Bitter Almond Oil. $C_6H_5.CHO$.

Colourless liquid. B. P. 179°. Sp. gr. 1·05 at 15°. Odour resembles that of bitter almonds. Very sparingly soluble in water (about 1 in 300), easily soluble in alcohol or ether.

It is easily oxidised to benzoic acid, even by exposure to air (the presence of hydrocyanic acid retards the oxidation by air, and is sometimes added for this purpose).

Like other aldehydes it gives Schiff's reaction, forms a crystalline compound with sodium bisulphite, and gives a silver mirror with ammoniacal silver nitrate, but it does not reduce Fehling's solution.

A solution in water or aqueous alcohol gives with phenylhydrazine acetate, immediately, a yellow crystalline precipitate of benzaldehyde hydrazone,

$$C_6H_5.CHO + N_2H_3C_6H_5 = C_6H_5.CH:N_2HC_6H_5 + H_2O.$$

The product when recrystallised from aqueous alcohol melts at 156°. This reaction is perceptible even in extremely dilute solutions.

When acted upon by aqueous caustic potash it yields potassium benzoate and benzyl alcohol,

$$2C_6H_5.CHO + KOH = C_6H_5.COOK + C_6H_5.CH_2OH.$$

Dissolve 27 parts potash in 25 parts water and shake well with 30 parts benzaldehyde; allow to stand for some hours, add a little water and extract with ether; the ethereal solution on evaporation yields the benzyl alcohol, and the aqueous solution contains the benzoate; on acidification of the latter benzoic acid separates.

Boiled with potassium cyanide in alcoholic solution it undergoes condensation to benzoin:—

$$2C_6H_5.CHO = C_6H_5.CO.CHOH.(C_6H_5).$$

Dissolve 5 parts potassium cyanide in 20 parts water and mix the solution with 25 parts benzaldehyde and 50 parts alcohol. Boil the mixture on a water-bath for about an hour (using a reflex condenser). The benzoin separates in crystals on cooling, and may be purified by recrystallisation from alcohol; it melts at 137°.

BENZOIC ACID.

$C_6H_5.COOH$.

White shining leaflets or needles. Easily sublimes on heating, giving irritating vapours which have a peculiar and somewhat characteristic odour. M. P. 121—122°. B. P. 249°. Volatile in steam. Very sparingly soluble in cold water (about 1 in 350 at 20°), fairly easily soluble in alcohol or ether.

Heated with alcohol and a little concentrated sulphuric acid it gives a fragrant odour due to ethyl benzoate.

Distilled with excess of soda-lime it yields benzene,

$$C_6H_5 . COOH - CO_2 = C_6H_6.$$

Grind together benzoic acid and about 4 times its weight of soda-lime; heat in a small flask or retort, condensing the vapours in a well-cooled U-tube. Separate the benzene from water, which may also come over, and examine as on page 126.

Solutions of benzoates (*e.g.* ammonium benzoate prepared by dissolving the acid in ammonia and boiling off the excess of ammonia) give with ferric chloride reddish brown ppt. of basic ferric benzoate $2Fe(C_6H_5CO_2)_3 . Fe(OH)_3$; this precipitate is decomposed when boiled with ammonia but the filtered solution does not then give a precipitate with barium chloride and alcohol. (Compare Succinic acid.)

Silver nitrate gives a white ppt. soluble in hot water.

SALICYLIC ACID.

ortho Hydroxybenzoic Acid. $C_6H_4(OH) . COOH.$

Colourless needles (from hot water), or monoclinic prisms (from alcohol). Sublimes at about 200°; if quickly heated to 220° it partly breaks up into phenol and carbon dioxide. M. P. 156°.

Very sparingly soluble in cold water (about 1 in 400 at 15°), easily soluble in alcohol, ether, chloroform, &c.

Heated with soda-lime it gives the odour of phenol,

$$C_6H_4(OH) . COOH = C_6H_5OH + CO_2.$$

Heated with concentrated sulphuric acid and a few drops of methyl alcohol it gives methyl salicylate (oil of wintergreen), which has a pleasant and somewhat characteristic odour,

$$C_6H_4(OH) . COOH + CH_3OH = C_6H_4(OH) . COOCH_3 + H_2O.$$

Ferric chloride gives a purple or violet colour even in very dilute solutions (1 in about 100,000). The colour is destroyed by mineral acids or by alkalis in excess. The isomeric *meta* and *para* hydroxybenzoic acids do not give this reaction. Salicylic acid gives the reaction also in alcoholic solution. (Distinction from Phenol.) Bromine water in excess gives a yellowish-white precipitate, said to be 'tribromophenol bromide' $C_6H_2OBr_3 . Br$.

ANILINE.

Phenylamine. $C_6H_5NH_2$. [*Primary amine.*]

Colourless highly refractive liquid; soon becomes red or dark coloured when kept, especially in presence of air. B. P. 182—183°. Sp. gr. 1·026 at 15°. The pure substance solidifies when cooled in a freezing mixture. M. P. −8°. Slightly soluble in water; miscible in all proportions with most organic solvents. The aqueous solution precipitates some metals from their salts, as hydroxides. It acts as a monacid base, combining directly with acids to form salts. The oxalate and acid sulphate are sparingly soluble; the hydrochloride is very soluble, and easily hydrolyses; $(C_6H_5NH_2 . H)_2PtCl_6$ crystallises in yellow needles.

An aqueous solution of aniline when treated with a few drops of a solution of sodium hypochlorite or bleaching powder gives an intense violet colour.

A still more delicate reaction consists in adding bleaching powder solution, and then a drop of ammonium sulphide; a rose-red colour is thus produced; this test will even indicate one part of aniline in about 200,000 parts of water.

Dissolved in strong sulphuric acid and a crystal of potassium bichromate added, an intense blue colour is obtained.

Aniline salts when treated with nitrous acid yield salts of diazobenzene; these when warmed, in aqueous solution, decompose rapidly, giving off nitrogen and leaving phenol,

$$C_6H_5NH_2 . H_2SO_4 + HNO_2 = C_6H_5N_2 . HSO_4 + 2H_2O$$

and

$$C_6H_5N_2 . HSO_4 + H_2O = C_6H_5 . OH + N_2 + H_2SO_4.$$

'Methyl-furil'* gives in an acetic acid solution of aniline, a brilliant green colour. [This reaction is characteristic of *primary amines*, especially of the aromatic series; aliphatic amines give the reaction only under certain conditions.]

[With chloroform and alcoholic potash the odour of phenyl carbamine is produced. See Chloroform.]

DIPHENYLAMINE.

$(C_6H_5)_2NH$. [*Secondary amine.*]

Colourless solid; crystallises in monoclinic plates. M. P. 54°. B. P. 310°. Nearly insoluble in water; easily soluble in alcohol or ether.

With acids it forms salts which are very easily hydrolysed by water; this fact may be illustrated as follows:—Add an alcoholic solution of the base to a little water, and then clear up the resulting turbidity by addition of strong hydrochloric acid; if the solution is now diluted with water the free base again separates.

A solution of diphenylamine in strong sulphuric acid (prepared by dissolving about 0·5 gram in 100 c.c. of pure sulphuric acid and adding 20 c.c. of water) gives an intense blue colour with nitrates or nitrites. The reaction is very sensitive, and is sometimes used as a test for nitrates or nitrites; many other oxidising agents, however, give a similar reaction.

Nitrous acid, under appropriate conditions, yields the nitroso-derivative $(C_6H_5)_2N . NO$.

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* See note page 149.

DIMETHYLANILINE.

$C_6H_5N(CH_3)_2$. [*Tertiary amine.*]

Colourless oil. B. P. 192°. Sp. Gr. 0·955 at 20°.

By action of nitrous acid it yields *p.* nitroso-dimethylaniline, the NO group replacing hydrogen in the benzene nucleus:—

$$C_6H_5N(CH_3)_2 + HNO_2 = C_6H_4(NO).N(CH_3)_2 + H_2O.$$

Dissolve 1 part dimethylaniline in dilute hydrochloric acid (2½ parts concentrated acid and 5 parts water) and add gradually a solution of sodium nitrite in calculated quantity (about 0·7 parts), keeping the mixture cold by means of a freezing mixture. The hydrochloride of the base separates in the form of yellow needles. The free base is obtained by addition of potassium carbonate and extraction with ether, from which it separates on evaporation in green crystals. It does not give Liebermann's reaction.

p. nitroso-dimethylaniline when warmed with a solution of ammonium sulphide, cooled, acidified with hydrochloric acid and a small quantity of ferric chloride added, gives a deep blue colour (Methylene Blue).

When boiled with caustic soda it gives rise to dimethylamine and *p.* nitrosophenol (quinone monoxime),

$$C_6H_4(NO).N(CH_3)_2 + H_2O = C_6H_4(NO).OH + NH(CH_3)_2.$$

The dimethylamine will be recognised by its ammoniacal, fish-like odour; the nitrosophenol may be extracted with ether (after acidification), and when mixed with phenol and a little concentrated sulphuric acid gives a red colour changing to blue on addition of caustic alkali. (See Phenol.)

PHENYLHYDRAZINE.

$N_2H_3(C_6H_5)$. [*Primary hydrazine.*]

Nearly colourless oil. Sp. gr. 1·107 at 10°. Solidifies in cold weather to a crystalline mass. M. P. 23°. Under ordinary pressure it boils with some decomposition at 242°, but may be distilled unchanged in steam. Slightly soluble in hot water, easily soluble in alcohol, ether, benzene, &c.

Combines with many acids to form salts; the hydrochloride $N_2H_3C_6H_5.HCl$ is fairly easily soluble in water or alcohol, the oxalate is only slightly soluble in water and insoluble in alcohol. For most reactions a solution of the acetate is used; this may be prepared by mixing phenylhydrazine with about an equal volume of 50 per cent. acetic acid (if a stronger solution is used crystals will separate). Or it may be prepared by mixing the hydrochloride (2 parts) with sodium acetate (3 parts) in water (20 parts); these reagents must be freshly prepared.

Reduces Fehling's solution, or cupric acetate, even in the cold giving a red precipitate of cuprous oxide, free nitrogen and benzene being also produced,

$$N_2H_3C_6H_5 + 2CuO = Cu_2O + C_6H_6 + H_2O + N_2.$$

With aldehydes, ketones and other compounds containing the CO group, it yields hydrazones: *e.g.* with pyruvic acid:—

$$CH_3.CO.COOH + N_2H_3C_6H_5 = CH_3C:N_2HC_6H_5.COOH + H_2O.$$

With many sugars it first yields hydrazones, but by further action the CHOH group (adjacent to CO) is oxidised, at the expense of part of the phenylhydrazine, and osazones result. (See Dextrose and Lævulose.)

ACETANILIDE.

Antifebrin. $C_6H_5 . NH(CH_3CO)$.

Colourless lustrous plates. M. P. 114°. B. P. 295°. Very sparingly soluble in cold water; easily soluble in alcohol, ether, benzene or boiling water. Combines with hydrochloric acid, giving a crystalline salt $[C_6H_5 . NH(CH_3CO)]_2 . HCl$, which is easily hydrolysed by water.

When boiled with concentrated hydrochloric acid or caustic alkalis it gives rise to aniline and acetic acid,

$$C_6H_5 . NH(CH_3CO) + H . OH = C_6H_5NH_2 + CH_3CO . OH.$$

By action of bromine it yields *p.* bromo-acetanilide $C_6H_4Br . NH(CH_3CO)$ which crystallises in colourless needles. M. P. 165°.

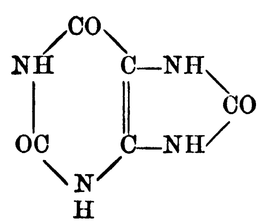
Dissolve acetanilide in glacial acetic acid, and gradually add rather more than an equal weight of bromine (also dissolved in glacial acetic acid). Allow to stand, pour into water, wash, drain and recrystallise from aqueous alcohol.

[Phenacetine (*p.* acetamidophenetol) $C_6H_4(OC_2H_5) . NH(CH_3CO)$ somewhat resembles acetanilide, but melts at 135°. It is distinguished also by the fact that a cold saturated solution does not become turbid on addition of bromine water and it gives somewhat different colour-reactions, *e.g.* with nitrous acid, chlorine water, ferric chloride, &c.]

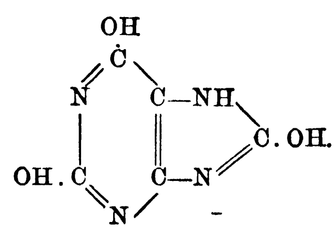
URIC ACID.

Trioxy-purine.

$C_5H_4N_4O_3$.



or



White crystalline powder. Nearly insoluble in cold water, alcohol or ether; very slightly soluble in boiling water (about 1 in 1800). Dissolves in alkalis, forming salts; dissolves also in concentrated sulphuric acid, and is reprecipitated by water. Soluble also in glycerol and in solutions of sodium acetate or sodium phosphate.

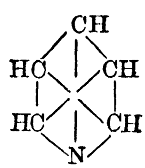
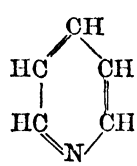
When heated it decomposes without melting, giving off hydrocyanic acid, ammonia, &c. and a white sublimate consisting of cyanuric acid, urea, ammonium cyanate and carbonate; a carbonaceous residue being left behind.

When a dilute solution of uric acid is mixed with a large excess of ammonium chloride (saturated solution) and allowed to stand for some time with occasional stirring, the very sparingly soluble acid ammonium salt is precipitated.

Evaporated to dryness with strong nitric acid (or with bromine water), on a water-bath, a yellow or red residue is left which when exposed to the vapours of ammonia assumes an intense purple colour; if caustic soda is now added the colour changes to blue. The purple compound is ammonium purpurate or *murexide* $(NH_4)C_8H_4N_5O_6$.

Alkaline solutions of urates reduce silver or copper salts; thus, a solution of uric acid in sodium carbonate gives a black stain with silver nitrate solution (*e.g.* on filter paper). Fehling's solution gives a greyish precipitate (said to be cuprous urate), or if warmed with excess of the reagent a red precipitate of cuprous oxide.

PYRIDINE.

C_5H_5N.  or  [*Heterocyclic compound.*]

Colourless liquid. Characteristic disagreeable odour. Poisonous. B. P. 116°. Sp. gr. 0·985 at 15°. Miscible with water and most organic solvents. Gives white fumes with HCl. The aqueous solution reacts alkaline. Tertiary monacid base.

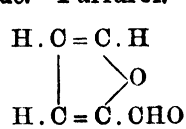
Precipitates hydroxides of Fe, Cr, Al from their salts. With copper sulphate it gives a pale blue precipitate which dissolves in excess to a deep blue liquid.

With hydrochloroplatinic acid it gives the salt $(C_5H_5N)_2H_2PtCl_6$ (orange prisms) which are fairly easily soluble; this, when its solution is boiled loses 2HCl, becoming $(C_5H_5N)_2PtCl_4$ which is a yellow insoluble powder. It gives crystalline compounds also with $HAuCl_4$ and $HgCl_2$, and (like alkaloids) gives precipitates with phosphomolybdic acid, picric acid, &c.

Boiling nitric acid does not oxidise it and its solution does not decolorise potassium permanganate.

FURFURAL.

Furfuraldehyde. Furfurol. Pyromucic aldehyde.

$C_4H_3O.CHO$ or  [*Heterocyclic compound.*]

Colourless liquid. Agreeable aromatic odour. B. P. 162°. Sp. gr. 1·159 at 20°. Moderately soluble in water. Easily soluble in alcohol. (Crude furfural slowly turns dark brown on exposure to light and gives a purple colour with strong mineral acids; these changes are due to impurity.)

Furfural (*continued.*)

With aniline acetate it gives an intense rose-red colour; the test is best applied on filter-paper.

With Schiff's reagent, Fehling's solution, sodium hydrogen sulphite, &c. it behaves like other aldehydes.

When its aqueous solution is boiled with silver oxide, metallic silver is deposited and the solution contains silver pyromucate, which on cooling separates in crystals. Alkaline potassium permanganate oxidises it similarly

$$C_4H_3O.CHO + O = C_4H_3O.COOH.$$

Boiled with alcoholic potash it yields potassium pyromucate and furfuryl alcohol. (Compare Benzaldehyde):

$$2C_4H_3O.CHO + KOH = C_4H_3O.COOK + C_4H_3O.CH_2OH.$$

The furfuryl alcohol may be removed by extraction with ether and the solution after acidifying and again extracting with ether yields pyromucic acid. The latter may be sublimed unchanged, and, when pure, melts at 134°.

When urea is dissolved in strong hydrochloric acid and mixed with an aqueous solution of furfural, a violet or purple colour is slowly developed.

Phenylhydrazine (or its hydrochloride or acetate) gives a yellowish precipitate of furfural phenylhydrazone $C_4H_3O.CH(N_2HC_6H_5)$ which crystallises from hot dilute alcohol in pearly scales. When carefully dried at 60—70° (best in a vacuum) it melts at 97°.

Methyl-furfural $C_4H_2(CH_3)O.CHO$ boils at 184—186°. With aniline acetate it slowly develops an orange colour. When concentrated sulphuric acid is carefully added to its alcoholic solution an intense green colour is produced.

ALKALOIDS.

This name is generally used in connection with certain organic nitrogen bases of more or less complex constitution which occur naturally, and have well-marked toxicological properties. They are usually optically active, crystalline (coniine and nicotine are liquids), insoluble or very sparingly soluble in water, but soluble in ethyl alcohol, amyl alcohol, chloroform or ether (morphine and narceine do not dissolve in ether). They dissolve in acids forming crystallisable salts, and are precipitated from the solutions by caustic alkalis (morphine dissolves in excess).

They give precipitates with the following reagents:—

Phosphomolybdic acid, phosphotungstic acid, potassium mercuric iodide, tannic acid, picric acid; these precipitates are white to yellowish-white or yellow. *Potassium bismuth iodide* gives an orange precipitate, and a solution of *iodine* in *potassium iodide* a brown (often crystalline) precipitate of the periodide.

QUININE. $C_{20}H_{24}N_2O_2$. Shining white needles. M. P. (anhydrous) 177°. Tertiary, di-acid base. Lævorotatory. Solutions of the sulphate, nitrate, phosphate or acetate exhibit a blue fluorescence which is destroyed by HCl, HBr or HI.

A solution of a quinine salt when mixed with a little chlorine or bromine water and then with ammonia in slight excess gives an emerald green colour changed to red by acids.

STRYCHNINE. $C_{21}H_{22}N_2O_2$. Colourless prisms. M. P. 284°. Tertiary, monacid base. Lævorotatory.

When dissolved in concentrated sulphuric acid, and a crystal or fragment of potassium bichromate is added, a blue or violet colour is obtained which soon changes to red or yellow. (Manganese dioxide, potassium permanganate, lead dioxide, &c. may be used instead of potassium bichromate.) The presence of brucine, quinine, morphine, &c. interferes with this reaction.

A minute quantity of potassium chlorate added to a solution of strychnine in warm dilute nitric acid gives a scarlet colour, changed to brown by ammonia.

BRUCINE. $C_{23}H_{26}N_2O_4$. Colourless needles or prisms. M. P. (anhydrous) 178°. Monacid base. Lævorotatory.

Dissolved in strong sulphuric acid, and mixed with a trace of nitric acid, or a nitrate, a deep orange-red colour is obtained. [Pure nitrites are said not to give the reaction if the test is applied carefully. See Nitrates.]

The colour may also be obtained by simply adding strong nitric acid to brucine. If the excess of nitric acid is removed by warming, and stannous chloride or ammonium sulphide is added, a violet colour is produced.

MORPHINE. $C_{17}H_{19}NO_3$. Crystallises in colourless prisms containing one molecule of water. Becomes anhydrous at 100°, begins to vaporise at 150°, and melts at 230°. Tertiary, monacid base. Lævorotatory. Dissolves in solutions of caustic alkalis, but scarcely in ammonia.

Ferric chloride added to a solution of a morphine salt gives a blue colour which is destroyed by acids or by heating.

Iodic acid added to a neutral or faintly ammoniacal solution gives a brown colour, due in part to the liberation of iodine; if starch solution is previously added a blue colour appears where the liquids meet.

Nitric acid gives an orange-red colour, changing to yellow. Chlorine water and ammonia give a red colour.

Heated with concentrated sulphuric acid to about 200° and poured into water a blue colour is obtained; chloroform shaken with this solution becomes blue, and ether becomes purple.

GLUCOSIDES.

These are compounds, which on hydrolysis yield glucose (or some other sugar), in addition, in most cases, to one or more compounds not belonging to the carbohydrate family. [In accordance with recent views the latter condition is not essential, since maltose for example may be regarded as glucose-glucoside, and yields only glucose or hydrolysis.]

Amongst the natural glucosides the following may be referred to as examples:—

AMYGDALIN. $C_{20}H_{27}NO_{11}$. Colourless prisms, containing $3H_2O$, from water or white shining leaflets from alcohol. M. P. 200°. Easily soluble in water or hot alcohol.

By boiling with dilute sulphuric acid, or by action of emulsin, it yields glucose, benzaldehyde and hydrocyanic acid.

$$C_{20}H_{27}NO_{11} + 2H_2O = 2C_6H_{12}O_6 + C_6H_5 . CHO + HCN.$$

SALICIN. $C_{13}H_{18}O_7$ or $C_6H_{11}O_5 . O . C_6H_4 . CH_2OH$. Trimetric tables. M. P. 201°. Very sparingly soluble in cold water, easily soluble in hot water or hot alcohol.

Treated with water in presence of emulsin or ptyalin it is hydrolysed to glucose and saligenin (*o.* hydroxybenzyl alcohol).

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_6H_4(OH) . CH_2OH.$$

A similar change is brought about when salicin is warmed with dilute sulphuric or hydrochloric acid, but in this case a portion of the saligenin undergoes dehydration, giving a product called saliretin (said to be $C_{14}H_{14}O_3$) which is a yellowish-white powder soluble in alkalis, but precipitated by acids.

The saligenin produced by the above hydrolysis may be recognised by oxidising the product with potassium bichromate and sulphuric acid, when some salicylaldehyde $C_6H_4(OH) . CHO$ is produced, and may be distilled off; this has the odour of 'meadow sweet,' and gives a violet colour with ferric chloride.

Strong sulphuric acid gives an intense violet-red or scarlet colour.

Glucosides (*continued*).

POPULIN. $C_{20}H_{22}O_8$ is benzoyl salicin. Silky needles (with $2H_2O$). M. P. 180°. Nearly insoluble in cold water, and sparingly soluble in boiling water.

When hydrolysed by dilute acids the products are dextrose, saliretin and benzoic acid; when boiled with baryta-water it yields salicin and benzoic acid. Emulsin does not hydrolyse it.

ARBUTIN. $C_{12}H_{16}O_7$. Colourless silky needles (with H_2O). M. P. 165°, or after fusion 187°. Easily soluble in boiling water or in alcohol.

By the action of emulsin or by boiling with dilute sulphuric acid it is hydrolysed to glucose and hydroquinone.

$$C_{12}H_{16}O_7 + H_2O = C_6H_{12}O_6 + C_6H_4(OH)_2.$$

Ferric chloride gives a transient blue or violet colour.

PROTEINS.

Complex colloidal substances. Composition somewhat variable (C. 50—55; H. 6·5—7·3; N. 15—17·6; O. 19—24; S. 0·3—2·4 per cent.).

General reactions. (These must be regarded as indications of the existence of certain groups rather than as specific properties of the 'molecule' as a whole.)

Xanthoproteic reaction. Heat substance with strong nitric acid; the substance turns yellow, and a yellow solution is formed; on addition of ammonia the colour changes to orange. The colour appears to be due to nitration in a benzene nucleus.

Millon's reaction. Mercury is dissolved in about an equal weight of strong nitric acid, the solution is diluted with twice its volume of water, and allowed to settle. On warming the clear solution with a proteid a brisk red colour is produced. This reaction is also given by phenol and by tyrosine; it appears to be indicative of an OH group associated with a benzene nucleus.

Adamkiewicz reaction. When a proteid is dissolved in glacial acetic acid containing a trace of glyoxylic acid, and strong sulphuric acid is gradually added, a violet colour is produced where the liquids meet. (Ordinary commercial glacial acetic acid often contains sufficient glyoxylic acid to give the reaction.)

'Biuret reaction.' Excess of caustic soda and a drop of copper sulphate gives a violet or pink colour analogous to that obtained with biuret (see Urea). The reaction is supposed to be due to complexes containing groupings similar to those in biuret.

Many proteids when dissolved in concentrated hydrochloric acid give a bluish or violet solution which fades or becomes more violet on warming.

Nitric, metaphosphoric, trichloracetic, hydroferrocyanic, phosphomolybdic, phosphotungstic, picric, and many other acids, alcohol and metallic salts (*e.g.* ammonium sulphate) cause coagulation or precipitation in solutions of proteids.

Molisch's reaction (see page 149) gives a result similar to that shewn by carbohydrates, and appears to indicate the existence of carbohydrate groupings or nuclei in proteids.

When boiled with caustic alkalis proteids yield a part of their sulphur as sulphide, which may then be detected by lead acetate. The total sulphur can be obtained in the form of sulphate by fusion with a large excess of a mixture of 8 parts KNO_3 to 1 part Na_2CO_3.

SUGGESTIONS FOR THE PRELIMINARY EXAMINATION OF UNKNOWN SINGLE ORGANIC COMPOUNDS.

BEARING in mind the enormous number of organic compounds already known (upwards of 200,000), the complexity of their constitution, and the fact that a large proportion of them shew no specific reactions, it is obviously impossible to formulate any general scheme of qualitative analysis which will be universally applicable for their identification.

It is possible in most cases to ascertain by means of general and typical reactions the class to which a given compound should be assigned; but even the attainment of this object is often a matter of no little difficulty, especially when groupings characteristic of more than one class are present. The complete identification of a given organic compound by qualitative methods alone is often impossible, and it then becomes necessary to determine the ultimate quantitative composition and molecular weight; the quantitative determination of groups (hydroxyl, carbonyl, acetyl, &c.) is also essential in many cases.

In the writer's opinion it is not advisable to attempt to lay down hard and fast rules as to the mode or order of procedure in qualitative organic analysis; in practice it will generally be found preferable to deal with each individual case as common sense dictates. The choice of tests and the order of their application will, as a rule, be clearly indicated after the first few initial observations.

The following directions merely indicate, in brief outline, a few of the general tests which are commonly used, and in addition, some of the reactions recently proposed by the writer have been introduced.

Carefully note the physical characters of the substance—such as colour, odour, crystalline form, solubility in various common solvents, action on indicators, &c.

Heat a small portion in a bulb-tube or test-tube and observe whether it appears to vaporise unchanged or to suffer decomposition, and whether any characteristic odour can be perceived.

Determine, if possible, the melting-point or boiling-point, or both. A specific gravity determination is also desirable if time allows.

If there appears to be any doubt about the purity of the given substance steps must be taken to purify it by recrystallisation from some appropriate solvent, or mixture of solvents, or by distillation, sublimation, &c. Repeat this treatment if necessary until the properties, *e.g.* the melting or boiling point, are constant.

Determination of the elements present.

Heat a small quantity of the substance on platinum foil; if it leaves a residue which refuses to burn away, even after strong and prolonged heating, a metallic element (or silicon) is probably present; in this case the residue is examined separately for metals, &c.

Carbon and *hydrogen* are detected by heating with oxide of copper. Mix the dried* substance with about 4 or 5 times its weight of *dry* cupric oxide and heat in a small hard glass tube. Evolution of carbon dioxide (detected by lime water or baryta water) shews the presence of *carbon*, and water condensing on colder parts of tube indicates *hydrogen*.

Nitrogen, *halogens*, *sulphur*, and *phosphorus* may, as a rule, all be detected by ignition with metallic sodium. Heat a small piece of clean-cut sodium in a small test-tube or bulb-tube until it begins to vaporise, then introduce a few fragments (or a drop) of the substance to be examined and allow the mixture to deflagrate strongly. The reaction is a violent one and the experiment requires care; in certain cases, *e.g.* with some nitro-compounds, explosion may occur. (In the case of very volatile substances the experiment must be so arranged that the vapours pass over the strongly heated sodium.) Cool and treat with a little alcohol to destroy unaltered sodium. Extract with water, filter if necessary, and examine portions of the solution as follows:—

(*a*) For cyanide (and therefore for *nitrogen*) by ferrous salt, ferric salt, and dilute sulphuric acid. (Prussian blue test; see page 38.) (This test is applicable for all organic nitrogen compounds except diazo salts, &c., which decompose at too low temperature.)

(*b*) For *sulphide* by sodium nitroprusside, lead acetate, or silver coin.

(*c*) For *halogens* by acidification with nitric acid, boiling, and adding silver nitrate. (Distinguishing tests page 60.)

(*d*) For *phosphorus* by adding excess of nitric acid and ammonium molybdate and heating.

If nitrogen and sulphur are both present some sulphocyanate may be produced, especially if an insufficient quantity of sodium was employed; in this case the solution after acidification with hydrochloric acid will give a red colour with ferric chloride.

Since cyanides and sulphocyanates may interfere with the tests for halogens, it is advisable, when nitrogen is present, to examine for halogens by one of the methods described below.

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* The method of drying must depend on the problem to be solved; if, for example, hydrogen present as water of crystallisation, or of hydration, is to be distinguished from hydrogen present as an essential constituent of the compound, the substance must be dried in a vacuum desiccator, in a water-oven or air-bath according to circumstances.

Halogens may be detected by heating the substance with pure lime or under certain conditions with pure sodium carbonate, and testing the product as above. The reagents should first be tested for purity. Organic compounds containing halogens when heated with oxide of copper in a Bunsen flame give a green or bluish-green colour, due to the vaporisation of copper halide. Halogens may also generally be detected by warming with excess of concentrated sulphuric acid, when either the halogen acid or the free halogen will be evolved.

For the detection of *halogens*, *sulphur*, and *phosphorus*, sodium peroxide has also been recommended. For this purpose the peroxide should be mixed with an excess of some substance rich in carbon and hydrogen such as naphthalene. A small quantity of this mixture is placed in an iron tube, a fragment or drop of the substance to be examined is added and heated strongly in a Bunsen flame. The product is tested for halogens, phosphate, and sulphate as usual.

A mixture of sodium carbonate and potassium nitrate may be employed instead of the peroxide mixture.

Nitrogen in many organic compounds may be detected by heating with an excess of soda-lime and confirming the evolved ammonia by the usual tests (odour, action on red litmus or on mercurous nitrate, &c.).

A mixture of magnesium powder and dry sodium carbonate may be substituted for metallic sodium in the above-described test for nitrogen by the cyanide method, but is perhaps less delicate.

Having ascertained the general physical characters of the substance under examination and the nature of the elements present, the behaviour of any or all of the following reagents may be investigated as judgement indicates.

Action of Acids.

Try the effects of the common acids, both dilute and strong, on the substance itself or on its solution. The following results, amongst others, may be looked for:—

Bases which are sparingly soluble in water may dissolve easily, forming soluble salts (*e.g.* alkaloids). Many basic substances will form salts which are crystalline, sparingly soluble, or otherwise easily identified. (*E.g.* aniline sulphate, phenylhydrazine hydrochloride, urea nitrate). In cases where the hydrochloride is more soluble and does not separate, the base may often be obtained as a well-crystallised platini-chloride by adding H_2PtCl_6 to the HCl solution (*e.g.* ethylamine).

The addition of an acid may cause the separation of *sparingly soluble acids* (*e.g.* salicylic, mucic, uric) from their salts; in such cases the resulting precipitate easily dissolves in alkalis. Phenols may similarly be separated and will dissolve in caustic alkalis, but scarcely in alkaline carbonates.

Boiling with hydrochloric or dilute sulphuric acids will bring about such changes as the inversion of cane-sugar, and the hydrolysis of esters, amides, glucosides, starch, &c. In such cases further steps must be taken to separate and identify the products.

Boiling with strong hydrochloric acid will decompose carbohydrates, often with production of some furfural which can be identified by means of aniline acetate paper, (see page 136).

Heating with strong sulphuric acid causes carbonisation in many cases (*e.g.* tartaric acid, cane-sugar, citric acid (slowly)). It causes evolution of carbon monoxide from the following acids:—tartaric, citric, formic, oxalic, malic, pyruvic, lactic (and other hydroxy acids) and from many other substances.

Heating with moderately strong nitric acid will generally bring about oxidation, and in some cases the products are easily identified (*e.g.* mucic acid from milk-sugar).

The action of fuming nitric acid will often give rise to nitro-compounds, especially in the case of aromatic compounds (benzene, toluene, phenol, &c.), which will separate when the mixture is poured into water. A mixture of strong nitric and sulphuric acids is more efficient for this purpose in most cases.

In certain cases the addition of acids may cause the development of characteristic colour changes. Strong sulphuric acid, for example, gives a scarlet colour with salicin; nitric acid gives an intense blue colour with diphenylamine, red with brucine, yellow with proteids, &c. [When mixing nitric acid with a solution, or liquid compound, a blue or green ring may sometimes be noticed where the liquids meet, which is due to nitrous acid formed by reduction; this is said to be a very sensitive reaction for alcohol.]

Action of caustic alkalis.

The substance, or its solution, is treated with excess of strong aqueous potash or soda in the cold and the mixture is afterwards heated.

If the substance dissolves much more easily in the alkaline solution than in water it is probably an *acid* or phenol; in such cases it will generally separate out again on acidification if the solution is not too dilute. (Acids will nearly always cause effervescence in sodium carbonate solution; phenols can usually be extracted with ether from an alkaline solution after saturation with carbon dioxide.)

The addition of caustic alkali may cause the separation of *sparingly soluble bases* from their salts; the product which separates may be solid (*e.g.* alkaloids) or liquid (*e.g.* aniline, phenylhydrazine). Or a sparingly soluble decomposition-product may separate (*e.g.* chloroform from chloral). In such cases the product which separates is collected (by filtration or by a separating funnel) washed and examined.

If the solution turns yellow or brown on heating *aldehydes* or certain *carbohydrates* are probably indicated; the odour of aldehyde-resin may also be noticed.

Evolution of ammonia on heating indicates amides, amino-acids or ammonium salts. Volatile amines (ethylamine, &c.) may also be given off from these salts.

The action of caustic alkalis if continued long enough may bring about the *saponification of esters, amides, anilides, ureides, nitriles,* &c.) Aldehydes may in some cases give corresponding acids and alcohols (*e.g.* benzaldehyde, furfural).

In order to investigate such changes and identify the products the substance is boiled with excess of strong aqueous potash, in a flask fitted with a reflux condenser, for about half-an-hour. (In certain cases a much longer period is necessary.) The result of this operation is that the alcohol, amine, &c., or ammonia is set free and the acid remains in solution as a potassium salt. The mixture after saponification is therefore submitted to distillation and the distillate is examined for volatile alcohols, amines, &c.; in some cases steam distillation is necessary (*e.g.* with aniline) or the product may be extracted by ether or other appropriate solvent. (Evaporation is sometimes necessary, see p. 123.) After removal of the alcohol, amine, &c., in this way, the residual solution is examined for acids. Sparingly soluble acids will separate out at once, or will crystallise out on standing, after the solution is acidified. Otherwise the solution, after evaporation to small bulk and strong acidification, is extracted with ether or is again submitted to distillation. In some cases the acid may be identified by qualitative tests in the mixture after saponification, neutralising and evaporating just to dryness if necessary*.

With certain substances it is advisable to repeat this saponification experiment, using (ethyl or methyl) alcoholic potash in place of the aqueous alkali. Fats and oils, for example, are much more readily saponified in this way. The action of alcoholic potash may also bring about further changes, such as the decomposition of halogen derivatives (chloroform into formate and chloride; ethylene dibromide into acetylene, &c.).

If the substance remains unaltered after the foregoing treatment with caustic alkalis and is also unaffected by aqueous acids, it is probably a *hydrocarbon*.

Paraffins will be recognised by their resistance to the action of a mixture of strong nitric and sulphuric acids; aromatic hydrocarbons will usually yield a nitro-derivative which separates when the mixture is poured into water. Or by treatment with fuming sulphuric acid the aromatic hydrocarbons will usually yield sulphonic acids which are soluble; on pouring the mixture into water the sulphonic acids dissolve and paraffins, being unaffected, will separate.

Saturated and unsaturated hydrocarbons are distinguished by the bromine test (see below).

Soda-lime.

The substance is well mixed with excess of soda-lime; the mixture is introduced into a hard glass tube, covered with more soda-lime and strongly heated.

Ammonia is evolved from a considerable number of organic nitrogen compounds.

Acetates yield methane; benzoates or phthalates (and salts of other benzene-carboxylic acids) yield benzene; salicylates yield phenol; formates yield hydrogen.

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* If the acid cannot be identified by its physical properties or its qualitative reactions, important information can generally be gained by determination of the equivalent weight (since equivalent weight × basicity = molecular weight). This can be done by analysis of its salts (*e.g.* silver salt) or by titration with standard alkali, using phenol-phthalein as indicator. The latter method, although quantitative, is of such a simple character that it may well be included in the qualitative scheme.

Bromine.

Dry bromine is dissolved in some inert solvent, such as carbon tetrachloride, and a few drops of the solution are added to the substance to be examined; this being, if possible, dissolved in the same solvent. (If the substance is a liquid a drop or two of bromine may be added directly to it.) The mixture is then warmed and more bromine is added if necessary.

If the bromine is rapidly decolorised without any evolution of hydrogen bromide, an unsaturated compound is probably indicated; [actual evolution will not take place if the substance combines with hydrogen bromide (*e.g.* amines) or if the selected solvent largely dissolves it].

If decolorisation takes place with evolution of hydrogen bromide, substitution is indicated. (It must not be forgotten that substitution and addition may occur together.) Special conditions (action of light, catalysers, &c.) are sometimes necessary in bringing about these changes.

Bromine water may give rise to similar results (sometimes more readily, *e.g.* with fumaric or maleic acids). Hydrogen bromide if formed will not be evolved in this case. But the action of bromine in presence of water may also bring about oxidation (*e.g.* aldehydes to acids), the colour of the bromine being discharged.

Bromine water when added to aqueous solutions may give rise to white or yellow precipitates of sparingly soluble bromo-derivatives; *e.g.* with phenol, salicylic acid or resorcinol, acetanilide.

Fehling's Solution.

To the aqueous solution of the substance (neutral or alkaline) add a few drops of Fehling's solution; allow to stand for a minute and then heat to boiling.

Reduction on heating may indicate *aldehydes* (not benzaldehyde), most *sugars* (not cane-sugar) and many other reducing substances.

Rapid reduction in the cold may indicate lower sugars (glyceraldehyde, dioxyacetone, glycollic aldehyde) hydroquinone, hydrazine hydrate, hydroxylamine, phenylhydrazine.

If a negative result is obtained the test should be repeated after hydrolysis with dilute acids, the free acid being of course neutralised before the test is applied.

Ammoniacal Silver Nitrate.

To the aqueous solution, carefully neutralised if necessary add ammoniacal silver nitrate (p. 33) and allow to stand.

Rapid reduction to a silver mirror, in the cold, probably indicates *aldehydes.*

But many other substances also cause reduction in the cold, sometimes with the formation of a mirror; *e.g.* hydroquinone, pyrogallol, pyrocatechin, phenylhydrazine.

A silver mirror on warming may be due to milk-sugar, dextrose, tartaric acid.

The reagent is more sensitive if a very little caustic soda is also added.

Schiff's Reagent.

(Solution of a rosaniline salt just decolorised by sulphurous acid.)

To the aqueous solution of the substance add one or two drops of the reagent and allow to stand for one or two minutes; if a pink (purple, blue, &c.) colour appears within this time *aldehydes* are probably indicated. Free alkalis must be absent; mineral acids make the test less delicate. Heating must be avoided. The reagent should be freshly prepared and should not contain large excess of sulphurous acid.

Ferric Chloride.

The reagent is added, drop by drop, to a cold aqueous solution of the substance (or in some cases to the solid shaken with water).

Nearly all hydroxy compounds give some sort of colour; the following are some of the commoner examples:

Hydroxy acids (aliphatic) give a yellow colour; with the α hydroxy acids this is especially well marked (*e.g.* lactic, tartaric, malic, citric).

A violet colour is given by phenol, salicylic and other *ortho*-hydroxy acids, resorcinol, phloroglucinol, salicyl-aldehyde, arbutin, acetoacetic ester and many other compounds.

Pyrocatechol and most other *ortho*-dihydroxy compounds give a green colour, which is changed to violet by alkalis.

Hydroquinone gives in the first instance, blackish-green lustrous crystals of quinhydrone, and on boiling with excess of ferric chloride, a pungent odour of quinone.

Morphine gives a dirty blue or green colour. Gallic acid gives a bluish-black precipitate.

A red colour is given by acetates, formates, sulphocyanates, oxalacetic acid, glycocoll, &c.

Potassium Permanganate.

This reagent will of course oxidise a large number of organic compounds, becoming itself decolorised, changing to green or giving a brown precipitate according to circumstances.

The instantaneous reduction in alkaline (sodium carbonate) solution is often used as a test for unsaturated acids (Baeyer's test), but many other substances behave similarly (formates, phenol, aldehyde, acetone, &c.).

Phenylhydrazine.

A dilute aqueous solution of the substance to be examined is mixed with a few drops of phenylhydrazine acetate solution (see page 133).

A white or nearly white precipitate is probably the *hydrazone* of an aldehyde or ketone (or aldehyde-acid, ketone-acid, &c.). Mannose also gives a hydrazone which is often more or less discoloured, but becomes nearly white on purification. (See Mannitol.)

A white crystalline precipitate may however be due to the formation of a sparingly soluble phenylhydrazine *salt* of the acid (*e.g.* oxalic acid). In some cases these can be distinguished by the fact that they are less easily formed when phenylhydrazine *hydrochloride* solution is employed in place of the acetate.

If no precipitation takes place in the cold the mixture is heated on a water-bath. An orange coloured precipitate which separates under these circumstances is probably an *osazone*, *e.g.* of a sugar. The osazones of monosaccharides (dextrose, lævulose, galactose, &c.) usually separate after a few minutes' heating; those of maltose and milk-sugar do not separate until the mixture, after sufficient heating, is allowed to cool. (Cane-sugar itself gives no osazone, but it becomes hydrolysed after the solution is heated for a long time and then yields glucosazone.)

The precipitate of hydrazone or osazone obtained in the above manner is collected on a filter, washed, recrystallised from some appropriate solvent, and its crystalline form examined; it is then dried and its melting point determined, usually by the 'quick-heating method.

If a negative result is obtained a portion of the original substance should be hydrolysed by boiling with dilute sulphuric acid, sodium acetate added, and the test repeated (*e.g* cane-sugar, glucosides).

Sodium Hydrogen Sulphite.

The liquid substance, or a strong aqueous (or ethereal) solution of the solid, is shaken in a stoppered bottle with a considerable excess of the freshly prepared reagent (see page 110) and allowed to stand for some hours. If a crystalline precipitate separates, an *aldehyde* or a *ketone* is indicated. The aldehyde or ketone may often be recovered from the precipitate by distillation with sodium carbonate or with an acid.

Oxidation with Chromic Acid.

The substance is oxidised by acting upon it with a mixture of chromic acid, or potassium bichromate, and moderately dilute sulphuric acid. The most suitable proportions and conditions vary considerably according to the nature of the case. The substance may be mixed with sulphuric acid and dropped on to the solid bichromate or chromic anhydride or in other cases the substance is gradually added to the oxidising mixture or *vice versâ*. The quantities should of course be calculated and adjusted according to the reaction desired. But even when the operation is performed in a rough manner without taking known proportions, there will generally be enough of some characteristic oxidation product formed to give useful information. The products are distilled off (or in some cases separated by extraction with ether, crystallization, &c.), fractionated if necessary, and identified by their properties and reactions.

It is easy in this way to recognise, for example, the formation of acetaldehyde from ethyl alcohol, acetone from isopropyl alcohol, valeraldehyde from ordinary amyl alcohol, acrolein from allyl alcohol, formic acid from methyl alcohol, &c.

For some purposes it is preferable to use acetic acid instead of sulphuric acid, *e.g.* in the oxidation of anthracene to anthraquinone.

Oxidation by means of Hydrogen Dioxide in presence of Iron.

A considerable number of organic compounds when carefully acted upon by hydrogen dioxide in presence of ferrous iron yield oxidation products which are characteristic and easily identified. (In absence of ferrous iron the actions here mentioned either do not take place at all or do so only to such a small extent that it is usually impossible to recognise the products.) As examples may be mentioned the oxidation of lactic acid to pyruvic acid, tartaric acid to dihydroxymaleic acid, malic acid to oxalacetic acid, glycol to glycollic aldehyde, glycerol to glyceraldehyde, mannitol to mannose, and many sugars to 'osones,' and other products. Aromatic compounds also are often oxidised, *e.g.* benzene yields some phenol, and benzoic acid gives some salicylic acid.

In order to apply this method for the identification of unknown substances, the oxidising agent must be added tentatively in limited amount since the initial products as a rule easily undergo further oxidation.

The substance to be examined is dissolved in water, mixed with a few drops of a solution of ferrous sulphate or acetate, and the hydrogen dioxide added drop by drop. In the case of acids it is necessary to carefully cool the mixture by ice during the operation; with polyhydric alcohols the temperature may be allowed to rise somewhat (say 40—50°), and in the case of carbohydrates it is generally advisable to warm the mixture on a water-bath. The proportion of hydrogen dioxide added should never exceed one atom of active oxygen for one molecule of substance, and it is usually safer to employ much less—(say 1 or 2 c.c. of '20 volume' H_2O_2 for 1 gram of substance). In the case of acids the oxidation is usually instantaneous, but with polyhydric alcohols and carbohydrates it is advisable to allow the mixture to stand for about half-an-hour.

A small quantity of the resulting mixture is now tested (with chromic acid and ether or with titanic acid) to ascertain whether any hydrogen dioxide remains; if this is the case the mixture is allowed to stand longer, or warmed, until the reaction of the dioxide is no longer given. But usually, if the presence of hydrogen dioxide can be detected after half-an-hour, it is probable that none of these 'typical' oxidations has taken place, and the test may then be abandoned.

Portions of the resulting mixture are then examined as follows:

(*a*) Ferric chloride is added.

An intense red colour (due to oxalacetic acid) indicates *malic acid.* A blackish or green colour which is changed to an intense violet on addition of excess of caustic soda indicates *tartaric acid* or *glyceric acid. Mucic* and *saccharic* acids also give a certain amount of violet or red colour under certain conditions, but the effects are very much less marked. There is usually enough ferric salt produced in the oxidation to give these effects to some extent, but they are greatly intensified by addition of ferric chloride. The colour given by glyceric acid is much less intense than that produced by tartaric acid, but the product is more stable; if the oxidised mixture is heated before application of the ferric chloride reaction, the tartaric acid product (dihydroxymaleic acid) will be destroyed, but the glyceric acid product (hydroxypyruvic acid (?)) will remain.

(*b*) A few drops of phenylhydrazine acetate are added and the mixture is warmed if necessary. The resulting precipitate is well washed, recrystallised from some appropriate solvent, and its crystalline form and melting point determined.

By means of these operations it is easy to identify many *polyhydric alcohols* and *hydroxy acids* of the aliphatic series.

(*c*) The oxidised mixture is heated nearly to boiling, a small quantity of phenylhydrazine *p.* sulphonic acid added and the heating continued for some minutes. The result of this experiment is that in certain cases dye-stuffs are produced. The product from tartaric acid, for example, will give a bright yellow dye, and that from *keto-hexoses* will dye silk an intense orange-pink colour which is very permanent.

Esterification.

In certain cases either *alcohols* or *acids* may be approximately recognised by conversion into an ester having a characteristic odour (*e.g.* ethyl or amyl acetate, methyl salicylate, ethyl benzoate).

For this purpose the acid, or its salt, may be heated with the alcohol and strong sulphuric acid.

The presence of OH groups is roughly indicated by the evolution of hydrogen chloride when the substance is acted upon by phosphorus pentachloride; it is of course important that the substance should be properly dried.

For the detection of alcoholic (or phenolic) *hydroxyl* the substance is acted upon by acetic anhydride, acetyl chloride or benzoyl chloride and the properties (melting point, &c.) of the resulting ester are determined. With acetic anhydride it is often necessary to employ catalysers, such as sodium acetate or zinc chloride. These actions are in many cases too elaborate for a rough preliminary examination of the kind now under consideration. But by the simple modification *Schotten* and *Baumann,* where the benzoylation is brought about in aqueous-alkaline solution, it is generally possible to obtain satisfactory results in a comparatively short time.

The substance is usually dissolved in water, mixed with an excess of benzoyl chloride and caustic soda and well shaken for several minutes at the ordinary temperature; any excess of benzoyl chloride is then removed by addition, if necessary, of more caustic soda and shaking until the odour of the reagent disappears. The proportions and conditions which are most suitable vary with different cases. (Take for example 0·5 to 1 gram substance, 5 c.c. benzoyl chloride and 25—30 c.c. caustic soda solution (10 per cent.).) The benzoic ester generally separates out a solid or as an oil which solidifies on standing. It is then washed, purified by recrystallisation and its melting point, &c., determined.

In addition to substances containing alcoholic or phenolic hydroxyl, primary or secondary amines may yield acetyl or benzoyl derivatives when subjected to the treatment above mentioned.

Molisch's colour-reaction for Carbohydrates.

To a dilute aqueous solution of the substance add a drop or two of a strong alcoholic solution of *a*. naphthol and then pour in carefully one or two c.c. of (pure) concentrated sulphuric acid. If carbohydrates are present, a violet or purple ring will be formed at the surface where the two liquids meet; the mixture may become red, blue or dark purple on shaking and when diluted with water a bluish-violet precipitate will separate. This reaction is supposed to be due to the formation of furfural and the action of the latter on *a*. naphthol. It is given by most sugars and by substances containing a carbohydrate nucleus (*e.g.* glucosides). If thymol is used in place of *a*. naphthol a deep red colour is obtained which on dilution with water changes to carmine; a flocculent carmine coloured precipitate afterwards separates.

Hydrogen Bromide test for Keto-hexoses.

A small quantity (say 10 c.c.) of dry ether is saturated, or nearly saturated, with dry hydrogen bromide, the solution is poured on to a fragment of the solid to be examined and the mixture allowed to stand. If an intense purple colour is developed within about 30—60 minutes it indicates *keto-hexoses* (*e.g.* lævulose, sorbose) or substances which yield these on hydrolysis (*e.g.* cane-sugar, inulin). The colour is due to the formation of bromo-methyl-furfural; if the operation is performed on a sufficiently large scale this product can be isolated in the crystalline form by neutralisation and extraction with ether.

'Methyl-furil'* test for Primary Amines, Ureas, &c.

A solution of the reagent in acetic acid gives with primary aromatic amines an intense green colour; strong mineral acids change the colour to yellow. (Primary aliphatic amines only give the reaction to a limited extent, and under certain conditions of concentration, &c.) The amine should be dissolved in acetic acid or in alcohol; the solution is then dropped on to filter-paper and tested with the reagent.

A minute quantity of urea when mixed with about an equal amount of the reagent and then treated with a drop of phosphorus oxychloride yields gradually, after a minute or so, a very brilliant blue colour. The phosphorus oxychloride may conveniently be dissolved in some inert solvent such as petroleum ether; acetyl chloride, dry hydrogen chloride, &c., may be used instead of phosphorus oxychloride. (The reaction may also be shown by dropping an aqueous solution of urea on to filter-paper which has been impregnated with a solution of the reagent and then adding concentrated hydrochloric acid; performed in this way the test is less delicate.)

Urethane, sodium carbamate and allantoin give a somewhat similar reaction; otherwise the test is specific for urea and mon-alkyl ureas.

With caustic alkalis or other solutions containing a sufficient concentration of OH' the reagent gives a beautiful blue-violet colour, which is destroyed by acids.

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* This name is given provisionally to a product obtained from bromo-methyl-furfural by the action of sulphurous acid. It is a crystalline substance having the molecular formula $C_{11}H_8O_4$. For preparation and reactions see *Trans. Chem. Soc.* 1899, *431*, and 1903, *187*.

General test for Hexoses.

All hexoses, and carbohydrates which yield them on hydrolysis, give a certain amount of bromo- or chloro-methyl-furfural when acted upon by the respective halogen acids under suitable conditions. The test mentioned in the last section but one, depends upon the fact that ketohexoses yield a very much larger proportion than aldohexoses. It happens that these halogen-methyl-furfurals give a very sensitive and characteristic reaction with ethyl malonate and consequently, this reaction serves for the identification of hexoses. There are various ways of carrying out the test. The following is an example.

A minute quantity of the solid substance to be examined is just moistened with a drop of water and is then boiled for about 3 or 4 minutes with a few drops of phosphorus tribromide (or trichloride) dissolved in a suitable solvent, e.g. in about 10 c.c. of toluene. The liquid is then poured off, cooled, mixed with a drop or two of ethyl malonate and made just alkaline with alcoholic potash. On diluting the mixture with alcohol and water, an intense *blue fluorescence* is obtained. (*Proc. Cambridge Philosophical Society*, 1907, XIV. 24.)

In addition to the foregoing tests many others may suggest themselves according to the nature of the results which have been obtained. For example:—Hofmann's isocyanide test for primary amines (also for chloroform, &c.), see page 104; Liebermann's test for nitroso-compounds (also for phenols), see page 128; nitroprusside reactions for amines, acetone, &c., see page 111; general tests for alkaloids and for proteid substances, see pages 136 and 138).

The action of *nitrous acid* will often afford valuable information, especially as regards the classification of amines. With primary aliphatic amines nitrogen is evolved at once; primary aromatic amines first give a solution of a diazo-salt in the cold, and on heating nitrogen is evolved, the resulting products (alcohols or phenols) are generally easily identified. Secondary amines yield nitrosamines which are generally insoluble and often yellow coloured, no nitrogen being evolved. Tertiary aliphatic amines are not acted upon, whereas tertiary aromatic amines give nitroso-compounds. See pages 132 and 133. Amides, amino-acids, &c., behave like primary amines, *i.e.* the NH_2 group is replaced by OH, with evolution of nitrogen.

The behaviour of *hydroxylamine* is especially useful for the recognition of aldehydic or ketonic groups, the :C:O being converted to :C:N·OH. The resulting compounds (oximes) are sometimes very characteristic, but special precautions are often necessary in bringing about the change. The substance in solution is usually mixed with a solution of hydroxylamine hydrochloride, and the calculated quantity of caustic soda or sodium carbonate, see page 111. In other cases an alcoholic solution of free hydroxylamine is employed; this may be conveniently prepared by action of sodium ethylate on hydroxylamine hydrochloride in molecular proportions. [Wohl. *Ber.* 1893, *730.*]

For the use of *semicarbazide* in the recognition of ketones and aldehydes, see Supplement, page 194.

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